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THE EFFECT OF HYDROGEN ON THE MECHANICAL PROPERTIES OF COLUMBIUM

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THOMAS Wendell WOOD

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THE EFFECT OF HYDROGEN ON THE MECHANICAL

PROPERTIES OF COLUMBIUM

APPROVED BY

R. D. Daniels

W. R. Upthegrove

C. A. Hunt

C. M. Shepherd

DISSERTATION COMMITTEE

ABSTRACT

The mechanical properties of columbium-hydrogen alloys, as a function of hydrogen content, temperature and strain rate, were investigated.

Hydrogen embrittles columbium even at concentrations below the limit of solubility. The concentration of hydrogen necessary to effect a given degree of embrittlement increases with increasing temperature in a roughly exponential manner. When not masked by a high ductile-brittle transition temperature caused by other factors (e.g. grain structure or other embrittling impurities), a restoration of ductility is observed at low temperatures. The ductility minimum occurs at about -78°C, which temperature appears to be that of hydrogen strain aging during the tensile test. The ductility minimum phenomenon is the result of a certain manner of variation of yield strength, strain hardening exponent and fracture strength with temperature, since these three variables define the stress-strain curve. The embrittlement associated with the presence of hydrogen can be removed by vacuum dehydrogenation.

Hydrogen solubility in columbium increases with increasing temperature. The hydrogen concentrations necessary

to cause embrittlement vary with temperature in a manner similar to that of the solubility but are somewhat less than the gross solubility. At hydrogen contents above the limit of solubility a second phase forms with a volume expansion of ten per cent. This expanded second phase constitutes pre-stressed Griffith cracks of (100) planes and is the evident cause of embrittlement.

At hydrogen concentrations below the limit of solubility hydrogen is believed to segregate at microcrack vertices during plastic straining. The repulsive forces consequent to the segregation increase the stress concentration at the crack vertices. The applied stress required for fracture is thus lowered. Theories based upon crack surface energy reduction and upon the stress concentrating effects of segregation lead to the same conclusions regarding the effects of hydrogen on fracture strength. It is found that the fracture stress of columbium decreases, with increasing hydrogen content, most rapidly at the strain aging temperature. It is at this temperature, during straining, that hydrogen is delivered at a maximum rate to microcracks by the dislocations.

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CHAPTER I

INTRODUCTION

There are two general classes of metals absorbing or occluding hydrogen (1). One class is composed of those metals into which hydrogen dissolves endothermically, such as iron; the other is composed of those metals into which hydrogen dissolves exothermically, such as columbium. A few materials exhibit a mixed or temperature dependent behavior (1). Hydrogen has been found to be a potent embrittling agent in metals. The embrittlement in the endothermic system iron-hydrogen has been of considerable economic importance, and has thus been thoroughly investigated.

Hydrogen embrittlement in exothermic systems has not been studied to any great extent as compared to the hydrogen embrittlement of iron and steel. A study of the columbium-hydrogen system was undertaken because of the growing commercial importance of columbium and because the characteristics of the embrittlement associated with the presence of hydrogen in this material are little known and less well

understood. It is believed that detailed studies of a number of metal-hydrogen systems such as the columbium-hydrogen system will help to determine the basic mechanisms of the embrittlement.

Columbium is a refractory metal with a density between those of iron and nickel. In view of the possible high strength-to-weight ratios obtainable through alloying, considerable work has been done in an attempt to formulate a strong alloy which does not exhibit the prohibitively rapid oxidation of pure columbium at high temperatures. Such a material would be of great use in advanced aircraft and other high temperature applications. With a thermal neutron cross section of 1.1 barns per atom for a mean neutron velocity of 2200 meters per second, columbium is also attractive as a material for use in nuclear reactors (2).

Columbium reacts exothermically with hydrogen (3), producing a solid solution at concentrations less than .025 weight percent at room temperature. At concentrations above a highly temperature dependent solvus a second phase is precipitated. Like many similar metal-hydrogen systems, this system exhibits a miscibility gap with respect to hydrogen solution. The columbium-hydrogen phase diagram according to Albrecht et al. (3) is shown in Figure 1 (see Chapter V for more information and a discussion of the significance of this phase diagram to the hydrogen embrittlement of columbium).

Albrecht found the "critical temperature" of the miscibility gap in the columbium-hydrogen system to be about

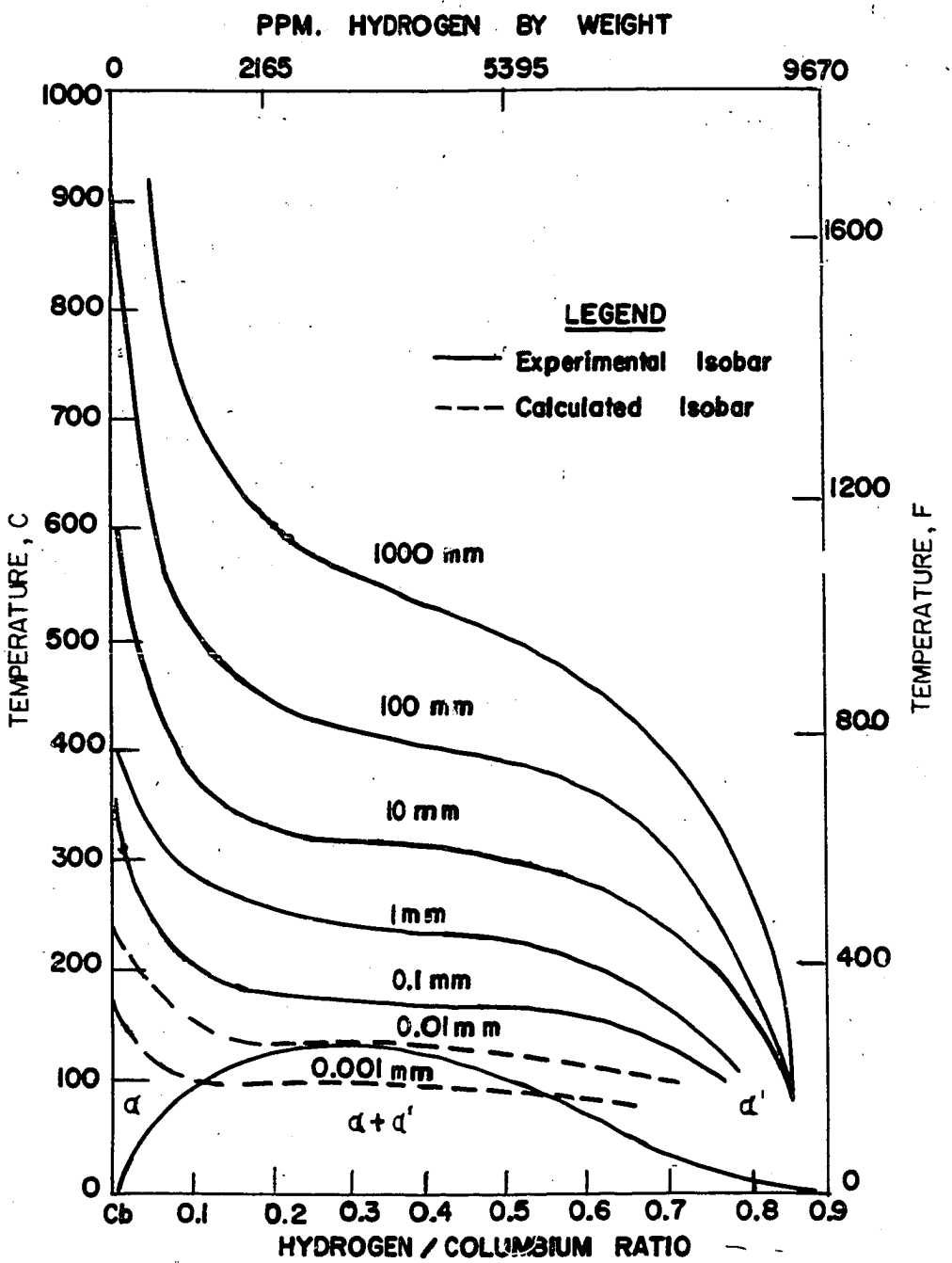


FIGURE I. THE PHASE DIAGRAM OF THE COLUMBIUM-HYDROGEN SYSTEM ACCORDING TO ALBRECHT ET. AL. (3)[a]

Equilibria and X-ray studies show that in the ranges 150° to 900° C, 0.1 to 1000 mm Hg pressure, and 0.01 to 0.85 H/Cb ratios, the columbium-hydrogen system consists of a single-phase body-centered Cubic structure. A two-phase region is present at relatively low temperatures and pressures with the critical point located at 140° C, 0.01 mm of Hg pressure, and 0.3 H/Cb ratio.

140°C, with a critical composition of .23 atom fraction hydrogen and a critical pressure of .01 mm Hg of hydrogen. Above 140°C there is a series of continuously expanding solid solutions across the phase diagram. Albrecht et al. found also that there was an expansion on precipitation of the second phase, from a lattice parameter of 3.30 Å at room temperature for the primary solid solution to a parameter of 3.41 Å for the expanded second phase at room temperature. At low temperatures the small atomic mobility of hydrogen inhibits its segregation into the second phase; an ordering has, however, been detected below -100°C. As temperature increases toward the critical temperature of the miscibility gap, however, the expansion of the columbium lattice on second phase precipitation must vanish. The second phase is a powerful embrittlement mechanism due to the strains produced by the expansion that occurs during its formation.

Albrecht and co-workers (3) obtained results different from those of Veleckis (4) in regard to the columbium-hydrogen phase diagram. Veleckis took thermodynamic equilibrium data from 300°C to 800°C and obtained a room temperature hydrogen solubility of 425 ppm as opposed to Albrecht's 250 ppm. Thus there is some disagreement in regard to the solubility of hydrogen in columbium.

Brief Survey of Hydrogen Embrittlement

Embrittlement is defined by Queneau as the loss of ductility without significant change in the other mechanical

properties (5). A change in ductility is usually accompanied by an apparent change in strength. For instance, an alloy addition which effects only solid solution hardening will raise the yield strength of a metal without affecting the fracture strength or fracture mechanism; so that fracture stress will be attained at a lower strain, and ductility will be reduced. Thus, there will be some who say that such a pure strengthening embrittles a metal.

An alloy addition may affect primarily the mechanism of fracture and cause a crack to traverse the specimen at a stress level lower than under other circumstances. Thus ductility in such a case will be reduced without a significant change in yield strength and one has an embrittlement according to Queneau's definition. Hydrogen embrittlement, although it varies in nature with the metal concerned, is primarily of this type.

The hydrogen embrittlement of steel has been of great economic importance and concern. Therefore, a large amount of work has been expended on it and the iron-hydrogen system. Whereas hydrogen does not notably increase the yield strength of steel, hydrogen greatly reduces the fracture stress of steel. The reduction in fracture stress due to a given amount of hydrogen is highly temperature dependent and exhibits a pronounced maximum in an intermediate temperature range. The disappearance of embrittlement at sufficiently reduced temperatures is attributed to the loss of mobility by the hydrogen atoms in the iron lattice so that the hydrogen

can not segregate to the fracture mechanism or crack initiation sites before the tensile specimen is broken. The disappearance of hydrogen embrittlement at sufficiently elevated temperatures is attributed to a reduced tendency for segregation to these sites, or the decomposition of the segregates if they had formed at a lower temperature. The embrittlement is in general greater under low rather than high rates of strain. This is interpreted as an effect of the limited mobility of the hydrogen atoms, fewer managing to segregate at the involved sites in the shorter allowed times at the higher strain rates.

A particularly dangerous form of hydrogen embrittlement occurs in alloy steels which are heat treated to high yield strengths. Such material may, while merely sitting on a bench, become honeycombed with cracks. Such damage results in catastrophic failure when the material is later subjected to loading. In this type of embrittlement it is evident that the time-consuming segregation of hydrogen is involved; the segregation being to sites that are operative as a result, perhaps, of the alloying and heat treating procedures used to obtain the high strengths.

In metal-hydrogen systems that occlude hydrogen endothermically, if hydrogen content is held constant and the temperature is lowered, the equilibrium pressure of diatomic hydrogen within any voids in the metal will increase to extremely large values. This fact has long been advanced

as a theory to explain the hydrogen embrittlement of this class of metal-hydrogen systems. A quantitative treatment is available (6). However this theory is somewhat complicated by such work as that of Hill and Johnson, who found that much of the hydrogen in steel is trapped in defects by sites of lower energy and not available for gaseous precipitation into microcracks.

In an exothermic occluder of hydrogen, the equilibrium pressure of hydrogen inside a microcrack decreases with decreasing temperature to the order of vacuum attainable by a good mechanical vacuum pump. In this instance the theory of Petch (7) appears to be applicable, wherein the absorption of hydrogen on a microcrack surface reduces the free energy of formation of the surface and gives rise to crack initiation at reduced applied stresses.

Brief Digest of Fracture Theory

There is a stress at which a perfect lattice, which remains perfect during the straining, will suffer fracture of the interatomic bonds so that a crack will traverse the specimen. This stress is termed the theoretical fracture stress. It cannot be accurately calculated since its dependence on the interatomic forces is not known accurately. However it is theoretically estimated to be about 10% of the elastic modulus (7), or 1,500,000 psi for columbium. The measured fracture stresses for all metals are one or more orders of magnitude smaller than this. Thus it has been

concluded that microscopic sharp cavities, called microcracks, which can provide the necessary large stress concentration factors to bridge the gap, are present in all metals at fracture.

These microcracks may be created during straining by the collision and coalescence of dislocations on intersecting slip planes, or by the agglomeration of dislocations at a grain boundary or other block on a slip plane, until the stress on the leading dislocations is sufficient to result in their merger. Then some of the remaining dislocations merge with these until a microcrack exists. Both these mechanisms, due to Cottrell (8) and Stroh (9) respectively, result in microcracks in the form of large dislocations. These concentrate stresses at their sharp ends. At some applied stress the concentrated stress becomes so large that the interatomic bonds are broken; once this situation occurs the higher stress associated with the enlarged crack is more than sufficient to repeat this process and the crack continues to grow across the metal. To provide a quantitative treatment, a free energy is provided for the microcrack, consisting of

1) the free energy of formation of the surface, plus
2) the elastic energy of the strain field about the microcrack, plus
3) the work done during plastic flow by dislocations moved by the magnified stresses near the crack vertex.

In ductile metals the third term may be of sufficient magnitude to stop crack propagation.

It is, of course, not necessary to have a microcrack present to produce fracture. If a localized small volume of a metal expands a few percent due for example to precipitation or impurity clustering, large stresses will be developed unless the segregate is sufficiently large to produce plastic flow. Such an expanded region can produce a stress resulting in crack initiation at a microcrack too small to otherwise produce fracture. This process of a precipitate particle "helping" a microcrack to initiate fracture is seen to be a powerful mechanism of embrittlement. Even with relief of stresses by plastic flow there is still a pre-stress of yield strength magnitude "frozen in" for a distance away from the particle. This situation will result in the reduction of the local applied fracture stress by an amount depending on the stress field produced by the expanded precipitate, the location and geometry of the adjacent microcracks, and other factors.

Objectives of Investigation

The objectives of this investigation have been:

1) To obtain the fracture and yield characteristics of pure and hydrogenated columbium over a wide range of hydrogen concentration, temperature and strain rate, for various conditions of history and analysis of the columbium.

2) To obtain insight into the physical mechanisms causing the observed behavior to the extent permitted by the incomplete state of development of the theory of mechanical properties.

CHAPTER II

PREVIOUS AND CURRENT WORK IN RELATED SUBJECTS

Little investigation of the mechanical properties of the columbium-hydrogen system had been done before the commencement of this investigation. A brief study is related in Corrosion Handbook (10). Concurrently Wilcox (11) did some complementary work on the Cb-H system. His previous strain aging study (12) is duscussed together with similar work of Begley (13) and Tankins and Madden (14) in Chapter VI as well as here. A brief account will be given here of each of the important works. A statement of the field of study of the authors will be given, followed by a summary of their results, and then criticisms which are considered pertinent.

Tankins and Madden (14)

Tankins and Madden studied the mechanical properties of purified columbium. Columbium wire of commercial purity was annealed in vacuum at 2000°C. The use of fairly high vacua and very high temperatures is required for the purification of columbium due to the reactivity of the metal. The use of ultra high vacua is impractical due to very low mass removal rates.

They concluded that columbium behaves in a similar manner to other body centered cubic metals in that yield point, strain rate sensitivity, and aging phenomena are exhibited. Work hardening of columbium does not occur at low temperatures and only an upper yield point was observed. The yield point obeys a $d^{-\frac{1}{2}}$ relationship. Twinning has been shown at liquid air temperatures. Columbium exhibits ductile properties down to liquid air temperatures providing that gaseous impurities are at a minimum.

Tankins and Madden found also that the strain-aging behavior of columbium exhibited an activation energy of 27,000 cal/mole, suggesting that oxygen is responsible. They suggest a dual mechanism for the yield point: First, the line dislocation is pinned by impurity segregates and when the dislocation becomes unpinned by pulling away from the segregates, a Frank-Read source can be set into motion. Second, the grain size dependence is then explained in terms of dislocations piling up at barriers, such as grain boundaries. The propagation of yield is then associated with the piled-up dislocations activating Frank-Read sources in adjacent grains.

A criticism that might be made of the work of Tankins and Madden is the use of .043" diameter wire for specimens, and the absence of a surface removal step from their procedure. Although great effort was made to obtain axiality of loading, with such a small gage diameter this is a difficult

problem. As they say, they had sufficient success in this to obtain sharp yield points in tantalum wire specimens. Also one has a problem of stress concentrations in cases of load transmittal to the specimen at locations where the specimen has the gage section diameter. The absence of a surface removal procedure raises the question of nonuniform contamination (which produced a yield point itself in our investigation) in heat treatments subsequent to their purification. Their work is in general, however, apparently of high quality.

In contrast to the work of Tankins and Madden, we did not observe twinning at liquid air temperatures. Our strain aging activation energy was different, but the Wessel (15) type explanation of the yield point advanced by Tankins and Madden was reinforced. Although in our investigation the presence of only an upper yield point at liquid air temperature was observed for material of the first heat, the yield point at liquid air temperatures disappeared completely in the recrystallized material of the third heat.

Balke (10)

Balke hung .004" sheet columbium in heated hydrogen, oxygen and nitrogen atmospheres, and measured the percent elongation of the strips of sheet in subsequent room temperature tensile testing. His gas contents were calculated from weight gain during the heat treatment. He concluded that 1000 ppm of hydrogen gave a partial embrittlement, percent elongation having dropped from 16% to 4½%. He also found

that "nitrogen penetrates the metal, whereas oxygen produces only a surface effect" in his treatments.

This last conclusion is contradicted by later more refined and thorough work (16). It is concluded there that air and oxygen are practically equivalent atmospheres, and that the nitrogen-columbium solution is formed at considerably higher temperatures than the oxygen-columbium solution due to diffusivity and reaction rate differences. Balke's hydrogen contents may be high due to impurity pickup from his hydrogen atmospheres, the purity of which is unspecified. Furthermore, resultant subsurface contamination would affect the mechanical properties. We found complete embrittlement by 1000 ppm hydrogen. His hydrogen distributions were uncontrolled as is seen from his treatment and weight gain data tabulation.

It is evident that Balke's work is not a sufficiently precise study of the Cb-H embrittlement to be useful in other than a qualitative sense.

Wilcox (11)

In this work, by B. A. Wilcox, A. W. Brisbane and R. F. Klinger, the strain rate and temperature dependencies of the low temperature deformation behavior of fine grained arc-melted columbium (1 ppm hydrogen) was evaluated for tensile strain rates of .005, 0.10 and 6.0 in/in.min. The effect of hydrogen content (1, 9 and 30 ppm H) on the mechanical behavior was also investigated in the temperature range 25 to -195°C, using a tensile strain rate of .005/min.

The existence of a hydrogen-dislocation interaction in columbium was concluded by means of:

1. Calculation of an apparent activation energy for the early stages of low temperature deformation

2. Observation of a hydrogen induced strain aging peak at -50°C, for columbium containing 30 ppm H, and

3. Observation of a serrated stress-strain curve at 25°C in coarse-grained columbium containing 89 ppm H.

Conclusion 2 is supported by our investigation. Conclusions 1 and 3 will be discussed later.

Wilcox's hydrogenation treatments were as follows. Half-inch rods were heated in flowing hydrogen at 1 atmosphere for specified times and then heated in flowing argon to homogenize the hydrogen contents in the gage sections of the specimens to be machined from the rods. However there was no calibration procedure to obtain controlled distributions. The gage sections of the broken specimens were analyzed for gas content by vacuum fusion analysis. Whereas this is good conventional procedure, the gas analysis results indicate that something was wrong.

Data on the diffusivity of oxygen (17) and the treatment data of Wilcox (11) show that diffusion of oxygen can not have penetrated in any significant degree into the gage sections of the to-be-machined specimens during Wilcox's hydrogenation and argon annealing treatments of the rods. The quantity $x//\overline{Dt}$, x being the difference in radius between

the rod and the future specimen, D being the diffusivity at that temperature, and t being the total time of annealing, is greater than 100 for oxygen, and, from nitrogen diffusion data (17) is some orders greater for nitrogen. Thus Wilcox's heat treatments satisfied the requirement that only the gage section hydrogen contents could be appreciably altered.

Also, from the vapor pressures of oxygen and nitrogen over columbium at these temperatures (18) (19) negligible amounts of nitrogen and oxygen could have been contained in the gas phase or removed from the hot zone. One can calculate the mass removal rate of a substance in a vacuum system from the ideal gas law. If S is the vacuum speed, P the vapor pressure of the substance of interest, M its molecular weight, R the gas constant, T the Kelvin temperature, and $\dot{m}$ the rate of mass removal of the substance of interest, then:

$$\dot{m} = P\ S\ M\ /\ R\ T$$

For P one has a quantity smaller than 10^{-26} atmospheres, for S one has a quantity which in the absence of trapping outside the hot zone for these permanent gases is no more than 10 liters/sec., and for M one has about 30 gms/mole. T is 675°K and R is 1/12. Thus one has a mass removal rate of less than 5×10^{-26} gms/sec. Thus Wilcox removed much less than 10^{-26} ppm of nitrogen from his columbium. One has then two bases for concluding that the changes in nitrogen (.065 down to .0085 wt %), oxygen and carbon analyses during Wilcox's hydrogenation and annealing treatments are due to errors in analysis or to material

inhomogeneity, which latter matter he did not mention. Since, furthermore, his hydrogen distributions are unspecified, one may question both the accuracy and distribution of his hydrogen contents.

In regard to his argon-annealing hydrogen homogeneization treatments, it might be remarked that Troiano (20) plates his material with cadmium, which is impermeable to hydrogen compared to iron and columbium, before homogeneization annealing, so as to improve results. A similar procedure with columbium would result in greater hydrogen retention and homogeneity in the gage sections.

Some differences in the results of Wilcox from those of Eustice and Carlson (21) and ours can be laid to Wilcox's analysis uncertainties as well as differences in impurity content and hydrogen distribution between the various investigators. Wilcox also observed twinning at liquid nitrogen temperature except in his most ductile material, tested at a strain rate of 6/min. This implies some strain rate, history and analysis dependence of the appearance of twinning during the tensile test. The transition temperature of ductility was observed to depend on strain rate also, the pure material being ductile at the highest strain rate at -196°C and brittle at the lower strain rates at this temperature.

In regard to conclusion 1, Wilcox calculates by a theory of Wert and Sinclair (22), (23) and activation energy for the low temperature deformation of columbium. Wert assumes that yielding is a thermally activated process,

exhibiting an activation energy that is increased by decreasing stress. Extrapolating to zero stress, Wilcox obtains an activation energy agreeing roughly with that of hydrogen diffusion in columbium (3), both in regard to his own data and that of another. It is not clear that he has enough data to give a firm conclusion. Since our temperature intervals are larger than his, we have not considered the calculations we could make to be of conclusive value. Our data does not conflict with Wilcox's conclusion of a hydrogen-dislocation interaction; we see a pronounced strain-aging-during-the-tensile-test at the appropriate temperature. Wilcox observes his strain-aging-during-the-test effect 25°C too high, and not until higher hydrogen contents than do we.

Wilcox notes that there is a small solid solution strengthening effect by hydrogen at low temperatures. This agrees with our results, although we did not observe more than a small strain rate dependence, over a 100 fold variation, in ductility.

Although Wilcox found a possible slight serration of the stress-strain curves at the temperature of the strain-aging-during-the-test effect, to obtain conclusion 3 he annealed a sample one hour at 1600°C in high vacuum and produced a grain size about 1/8 of the specimen gage section diameter. Pulling this large grained specimen at room temperature at a strain rate of .005/min. produced a serrated stress-strain curve of more pronounced serrations. However,

the serrations are supposedly produced by the alternate pinning and freeing of line dislocations by Cottrell atmospheres, at the temperature where the diffusivity of the atmospheric constituents is almost too low for the atmospheres to adjust to the motion of the dislocations (17). Thus this effect should be seen only at the temperature of the strain-aging-during-the-tensile-test peaks in strength and strain rate dependence of the strength. On the other hand, as the grains are nonuniformly deformed during the tensile test and the slip planes rotate nonuniformly and the distances along the planes between grain boundaries change nonuniformly, one would expect variations in flow stress with respect to time and the individual grains, with the result that there would be variations with strain in yield strength of the specimen, and thus serrations in the stress-strain curve. For a very small grain size, in which case the average flow stress would vary little over the specimen, one would expect the serrations from both the strain-aging and grain size sources to be cancelled out so as to produce a practically smooth stress-strain curve; but with a large grain size both effects would be expected to be visible. Thus one wonders if the effect that Wilcox observed by annealing to a large grain size is due to the grain size itself rather than the strain aging effect which should not be observed at that temperature.

In closing it might be said that the results of Wilcox complement ours in a field of great breadth. The mechanical properties of hydrogenated columbium depend on many

factors. There are some differences between our results and his, such as the absence of low temperature (-196°C) twinning and some similarities, such as the strain-aging-during-the-tensile-test effect. Wilcox observes a fracture stress minimum at -150°C for a hydrogen content of 30 ppm H, and an increase in the transition temperature of ductility on hydrogenation; but he might, as he says, have observed a low-strain-rate hydrogen embrittlement in his high-strain-rate, low-temperature ductility return rather than an adiabatic heating in the specimen. (This latter possibility was mentioned in his preprint, but not his paper.) But considerations of experimental procedure weaken his results and some of his conclusions appear dubious. Finally, his calculation of an apparent activation energy for the early stages of deformation of columbium at low temperatures appears to be unreliable due to the small number of data points involved and the apparent magnitude of the scatter.

Eustice and Carlson (21) (first paper)

In this paper Eustice and Carlson presented the results of an experimental study of the effect of hydrogen on the ductility of vanadium-columbium alloys. A phenomenological investigation was made of the effect of temperature and composition on the ductility of hydrogenated V-Cb alloys. All alloys in the system were ductile over the entire temperature range of -196°C to 25°C when hydrogen was not present. At a hydrogen concentration of 10 ppm, alloys containing up to 60 w/o

Cb exhibited embrittlement over varying temperature ranges while alloys of greater than 60 w/o Cb required greater amounts of hydrogen to produce hydrogen embrittlement. Pure columbium was embrittled by 20 ppm hydrogen which produced a ductility transition at approximately -70°C as determined from tension tests. They also found twinning in Cb at liquid nitrogen temperature. By bend testing they found that Cb with 10 ppm H retained full ductility down to liquid nitrogen temperature, whereas 50 ppm hydrogen produced a -25°C transition temperature.

There is some question in regard to their 1/8" gage diameter of their tensile specimens and their hydrogenation procedure. In regard to their hydrogenation procedure they have not shown that they have excluded impurities (they treated finished specimens) and that they have specified their hydrogen distributions.

Eustice and Carlson (24) (second paper)

In this study Eustice and Carlson determined the effect of hydrogen on the mechanical properties of iodide vanadium. They found that small amounts of hydrogen produce embrittlement of iodide vanadium metal over a limited temperature range. Data from slow tension tests showed a ductility minimum at approximately -100°C for metal containing 10 ppm of hydrogen. The temperature of minimum ductility was dependent upon hydrogen concentration and strain rate. Hydrogen raised the yield stress of vanadium quite markedly in the embrittled temperature range. The brittle behavior

of vanadium at these temperatures was attributed to this yield point phenomenon.

Eustice and Carlson found a more severe strain-aging-during-the-tensile-test effect in vanadium, which is immediately above columbium in the periodic table, than we found in columbium. This implies a stronger hydrogen-dislocation interaction in vanadium than in columbium. They attribute the embrittlement in hydrogenated vanadium primarily to this strengthening.

However Eustice and Carlson did not consider the effect of hydrogen on fracture stress. The yield stress, the strain hardening exponent, and the fracture stress determine the ductility of a metal; see Chapter VI. The fracture stress is that true stress at which a crack is observed to traverse the gage section of the specimen. Although the determination of this stress becomes quite difficult in cases of high ductility, in cases of low ductility fracture stress is an experimentally valuable quantity. The effect of hydrogen on the ductility of vanadium will be determined by its effect on these three independent variables. Thus any discussion of the effect of hydrogen on the ductility of a metal should include treatment of all three variables, or a set shown to be more fundamental. That part of their data which is relevant to fracture stress shows a fracture stress minimum at the strain aging temperature, which is our observation for hydrogenated columbium.

In regard to their experimental procedure one might note their 1/8" gage section diameter, their large grain size (1/2 mm) in regard to scatter, the annealing of finished specimens in recrystallization and hydrogenation, and lack of specification of their hydrogen distributions. Thus it does not appear that their data is of high accuracy and that it is discussed properly.

Strain Aging Work (17, 13, 12, 14, 25)

Begley (13) studied the kinetics of strain aging in columbium by determining the aging times and temperatures for yield point return after straining. Three specimens with interstitial contents of .06 w/o oxygen, .01 w/o nitrogen and .015 w/o carbon were recrystallized to ASTM 5 grain size. Tests were conducted at low temperatures and a "hard" tensile testing machine was used to minimize the distortion of the yield point by machine characteristics. The data was not very conclusive, but a value of 27,000 cal/mole for the activation energy of the return of the yield point on aging was obtained.

Dyson (25), as well as Begley, observed the serrated stress-strain curve at a temperature suggesting, as does Begley's strain aging data above, that oxygen is the element responsible for strain aging in columbium.

Wilcox (12) strained and aged four specimens of columbium in an air furnace between 120 and 260°C. The original interstitial contents were lower than for Begley's material.

Wilcox's material was recrystallized to 700 grains/mm^2 and subjected to hydrogen anneals. The tensile testing was done at low temperature, as for Begley, in a "hard" machine. Wilcox obtained an activation energy for return of the yield point on aging of 10,500 cal/mole. He also studied the changes of the dynamic modulus after compressive deformation in pure and hydrogenated columbium as a function of aging temperature. This study produced an activation energy of 8000 cal/mole. Thus in two ways hydrogen is indicated as the strain aging controlling agent, its activation energy for diffusion being 9.4 kilocalories/mole (3).

In regard to Wilcox's work several comments can be made. The remarks in regard to gas analyses apply somewhat more strongly than in the case of his mechanical property work (11) due to the large changes noted in oxygen and nitrogen contents. He indicates no correction for thermal relaxation time of the tensile specimen; assuming that two minutes should be deducted from his aging times produces a better fit of the data to a straight line and raises the activation energy to 12 kilocalories per mole, further from the 9.4 of hydrogen diffusion. There is some question, in view of his very large hydrogen content which forced him to reduce the compressive deformation prior to the dynamic modulus measurements, whether this hydrogen content reduced the accuracy of his measurements by internal cracking. He attributes the greater scatter of the dynamic modulus data to the second phase in the hydrogenated material, which is another

inhomogeneity. But the most interesting question seems to be why, if the hydrogen can keep up with the dislocations at conventional strain rates at 200°K, he must age at 400°K and above to restore the segregation into a Cottrell atmosphere, at which temperatures the diffusivity is considerably more than 100,000 times larger than at 200°K.

Begley's data indicating oxygen as the controlling element is less conclusive than Wilcox's and evidently conflicts more with the requirement of correction for specimen thermal relaxation time. However the data of Tankins and Madden (14) is much less uncertain in this respect and likewise implies oxygen.

Our data on three specimens with about ¼, 4½ and 8½ ppm hydrogen from the recrystallized third heat material gave an activation energy of 18 kcal/mole without hydrogen and 22 with hydrogen, with a 10^3 fold increase of the constant factor in the Ahrennius reciprocal aging time equation,

$$\frac{1}{t} = A \exp(-Q/RT)$$

where t is the aging time for return of the yield point at the absolute temperature T, and Q is the activation energy, and A is the constant factor. Thus we fall between the two conflicting results. An explanation rationalizing all these data may be obtainsble from the Wessel yield point concept as noted in Chapter V .

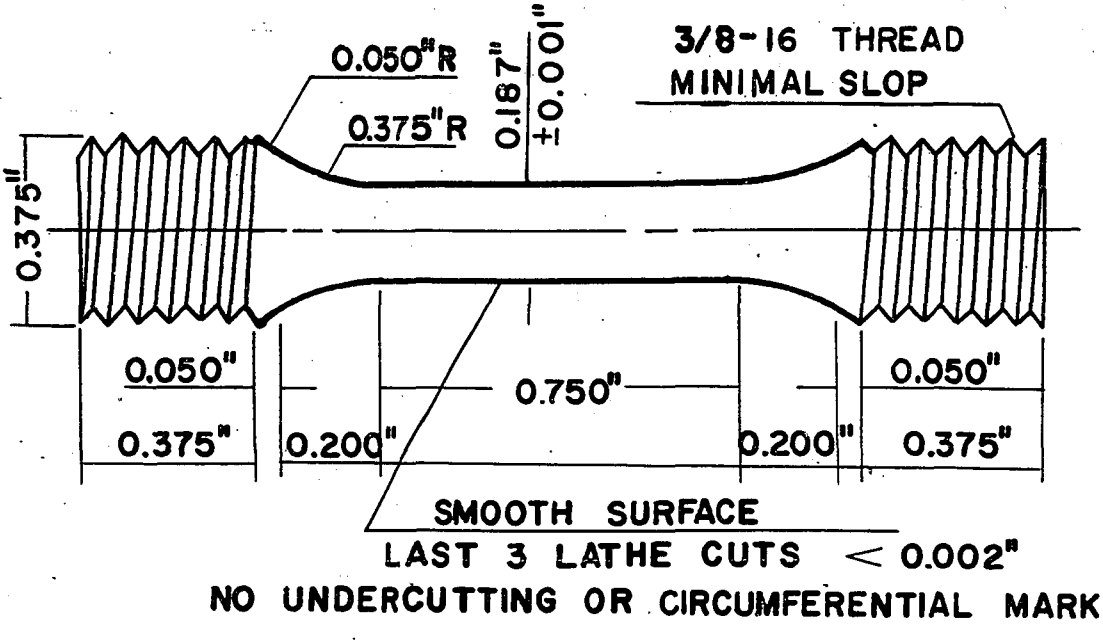
CHAPTER III

TEST METHODS

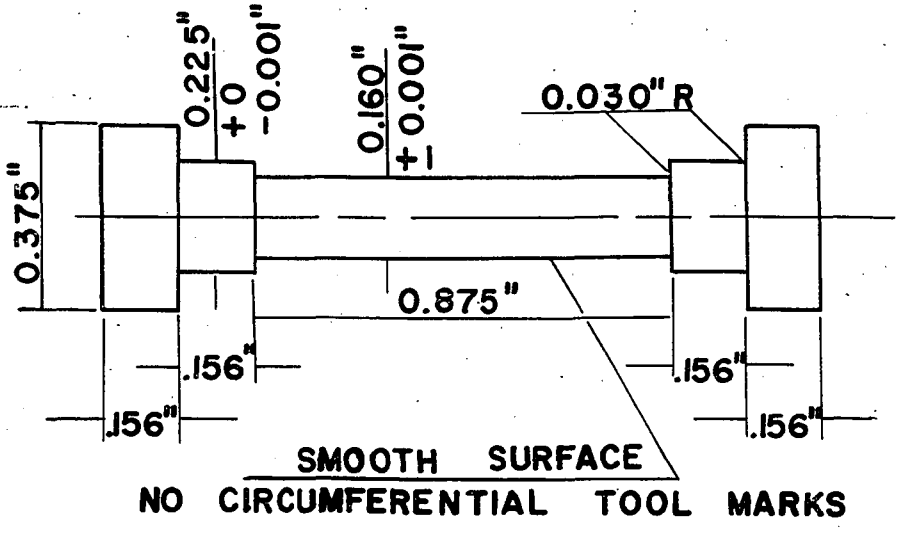
Specimen and Grip Designs

The Tensile tests were performed on an Instron testing machine. This machine records loads up to 10,000 lbs. and produces an accurate engineering stress-strain curve on a strip-chart. The test specimens employed are indicated in Fig. 2. One design is button-head and the other is threaded. The threaded design was used for tests on the first heat of columbium and the button-head design for the later lots of the material.

If the applied load on a tensile specimen is not coaxial with the axis of symmetry of the specimen there is a resultant error in the mechanical property data obtained from the test. The errors attendant to this "anaxiality" are determined by fabrication care and gage diameter. For a given order of tolerance the errors vary inversely as the gage diameter. The principles of tensile specimen design are discussed in handbooks (26;27). It was evident from study that specimens of a gage diameter smaller than that employed should not be used. To further minimize axiality



THREADED SPECIMEN - LENGTH 2.00" - SCALE 2.5:1
TOLERANCE ± 0.002 EXCEPT WHERE OTHERWISE NOTED



BUTTON HEAD SPECIMEN - LENGTH 1.50" - SCALE 2.5:1
TOLERANCE ± 0.002 EXCEPT OTHERWISE NOTED

THE TWO TENSILE SPECIMENS USED ON THIS PROJECT. REFS. 26 & 27

FIGURE 2

error the grip shafts were made as long as the testing machine permitted.

Button-head specimens are less susceptible to breakage in the gripping section than threaded specimens. This is an important consideration when the material being tested is notch sensitive. Failure of a threaded specimen in the gripping section will incapacitate a set of threaded grips. On the other hand threaded grips are much less expensive than button-head grips.

A total of 162 round and 38 sheet tensile specimens from three heats of columbium were pulled in the course of the investigation.

Procedure for High and Low Temperature Tests

The Instron testing machine was adapted for low temperature tests by surrounding the test sample with a refrigerant container. The container was an insulated can and the desired temperatures were obtained by use of a number of refrigerants. The refrigerants were liquid air, dry-ice-alcohol and ice-and-water. The insulation was removed, a lower grip shaft soft-soldered to the can base and the insulation replaced. The bath temperature was measured with an iron-constantan thermocouple and a portable potentiometer. The thermel was against or near the specimen surface and a decreasing-to-constancy of the bubbling of the bath, indicating thermal steady state, was awaited before the test was begun. The bath level was kept well above the top of the specimen.

For high temperature tests a vertically mounted, swinging tube furnace was swung out and the assembly of specimens and grips was inserted up the firetube, and secured into the upper machine socket as the furnace was swung back. Temperature control was maintained by a portable West on-off controller. A thermocouple, gently wired to the gage section, operated a relay in series with the furnace winding when the desired temperature limit was transgressed. Pyrex wool insulation was stuffed into the top and bottom of the furnace tube to obtain proper control. It was found that too much insulation or too high a winding voltage produced excessive overshoot. Thus the vertical tube furnace was run off an adjustable transformer at a low setting and insulation was similar in amount and compaction from run to run. The specimen was pulled when the temperature stabilized at the control point.

At the higher temperatures (up to 750°F) a layer of oxide formed which was blue or tan (a fraction of a micron or less in thickness). A control test indicated no loss of ductility from this development, as one would expect above the ductility transition temperature. On annealing a specimen at 950°F for 1 hour a dark blue tarnish formed on the specimen surface and yellow Cb_2O_5 powder was produced. This resulted in no measurable change in ductility. At low testing temperatures however, if an oxidized surface were at hand some loss of ductility would have resulted, and the machined

surface of the tensile specimens evidently resulted in a rise of several degrees in ductility transition temperature, judging from work on tungsten. An electropolished surface results in the greatest ductility, but will not be encountered generally in practice (29).

Hydrogen loss in high temperature tests was shown to be negligible by dehydrogenation runs described later. Room temperature testing was conventional and need not be described except to note that detailed precautions in the interest of accuracy were taken.

Curve Processing

The Instron testing machine provided strip-chart recordings of the load on the specimen vs. chart travel. From this record the engineering stress-strain curve could be obtained by converting the corrected chart co-ordinates. These curves and other data were processed to give at least six quantities: .2% yield strength, per cent reduction in area, proportional limit, tensile strength, per cent elongation and estimated fracture strength. When a yield point occurred the upper and lower yield strength, pre- and post-yield strains, and yield point height were recorded. One can obtain also the strain hardening exponent from a simple formula (30).

The accuracy of load measurement was better than ½%. The load measuring system was balanced and calibrated before and after each test, and the data corrected by interpolation if a detectable drift was observed during the test. The

accuracy of crosshead travel measurement was good due to control by a synchronous motor. Initially the strip-chart record rose slowly due to plastic mating of the load-bearing surfaces and slippage. Then in nearly all cases there followed a Hook's law section of considerable length and practically perfect straightness. This line was extrapolated to zero and full-scale load and plastic strain measured therefrom. This process was considered as accurate as an extensometer. The Instron manual cautions, however, that an extensometer should be used in the measurement of elastic modulus. The slope of the Hook's law section of the strip-chart is determined by the elastic moduli of the grip and machine, as well as specimen, materials, and geometry. The deflection of the machine and button-head grips was determined as 14.5-15 milli-inches per thousand pounds load.

Experimental Quantities

The first detectable deviation from the Hook's law straight line section is taken to mark the proportional limit. This quantity consequently corresponds to a .01-.02% yield strength. It is not so accurately determinable as the .2% yield strength and its error is about half again as great.

The .2% yield strength is accurately determined by carefully measuring from the extrapolated Hook's law section. The tensile strength is given by the maximum load ordinate divided by the original area. The fracture strength is given by the break in the pen line at specimen failure. In cases

of great ductility this break was gradual and failure occurred in a ductile rather than a Griffith manner. The experimental difficulties in the measurement of fracture strength are discussed in a later section. In the range wherein one is practically concerned with fracture strength (moderate and small ductility), fracture strength is determinable with proper accuracy.

The percent elongation was determined from the strip-chart. The percent reduction in area was determined by rotating the ends of the broken specimens in an optical comparitor and estimating the neck diameter several times, then averaging to obtain an approximate neck diameter. The conventional method of determining reduction in area will not work with ductile specimens as final area is small and Griffith fracture is often not attained. The percent elongation was taken as 100 times the engineering strain or fractional elongation as determined from the chart. This quantity could be obtained quite accurately. The value thus obtained is slightly smaller than that which the conventional method of fitting the broken ends together would produce due to fitting errors. See reference 28 for the conventional methods.

The quantities yield strength and fracture strength have been found to be the more significant strength variables. Reduction of area is considered to be a better determinant or measure of ductility than percent elongation.

Ductile failure and the central crack (31), convolution of the fracture perimeter and the considerable microscopic

and macroscopic inhomogeneity in the neck complicate the interpretation of fracture strength as the critical stress level of interaction of a uniform applied stress with a set of uniform microcracks, in cases of considerable ductility. However the observed trends are reinforced by correction for these effects. The experimental fracture strength surface over the temperature-hydrogen content plane is thus bent upward in regions of low hydrogen content and high temperature, deepening its minima.

The data presented is primarily confined to the more significant quantities of .2% yield strength, fracture strength and percent reduction of area. The complete test data may be found, together with a much more complete discussion, in a limited edition progress report and subsequent reports in single draft (30).

CHAPTER IV

HYDROGENATION PROCEDURE

Introduction

The most accurate and reproducible method for charging hydrogen into samples of a metal is to use a closed-system equilibrium technique. Consequently previous investigators who had suitable gas analysis systems at their disposal used them for charging. Having no such system, but choosing to use this more accurate if more time-consuming technique to charge columbium with hydrogen, a suitable system was designed and built. The principle of operation was simple: A quantity of hydrogen is initially measured by means of the ideal gas law. Part of this hydrogen is sorbed into the material and the remaining hydrogen measured. One then, at equilibrium, has a uniform and accurately known hydrogen distribution. The use of columbium rods from which the specimens are later fabricated permits the easy elimination of a nonuniform contribution to the hydrogen distribution on cooling as well as specimen contamination from impurity gettering. However the application of vacuum physics and considerable care in design and procedure is required. A condensed description of the apparatus and hydrogenation procedure follows.

General Operation

Before hydrogenation of the rods the hydrogen is confined in a reservoir consisting of a five-liter round-bottom pyrex boiling flask fitted with a 15 mm stopcock. The hydrogen was originally obtained from a commercial cylinder. It was gettered into columbium machining chips in a chamber consisting of a vycor tube standing in a copper rod above a Bunsen burner. The chips were cooled and the unreacted gases evacuated. On reheating these chips provide purified hydrogen. The pyrex-boiling-flask reservoir, which has a carefully measured volume, then containing an accurately known amount of purified hydrogen, is combined with an evacuated furnace tube containing the preheated rods of columbium. The hydrogen is sorbed into the rods. When the pressure stops falling one has an equilibrium state of uniform hydrogen concentration with a known amount of hydrogen unabsorbed.

After an equilibrium is reached between the absorbed and unabsorbed hydrogen, the samples are quenched. The quenching procedure consists of removing the furnace from around the fire tube. Unless the rods are too hot, the quench pickup is so small and so near the surface of the rod that the gage sections of the specimens to be made from the rods are unaffected in hydrogen distribution. Impurity contamination is similarly eliminated from the specimen gage sections by the low diffusivities compared to hydrogen of oxygen, carbon and nitrogen (16;17), and elements of greater atomic size. One removes the rods and has them machined within two weeks if

the quench enrichment was appreciable. The hydrogen-sorption vs. time curve for each run, together with relevant information such as surface treatment, has been presented (30). These data provide a useful tool for flow-past methods of hydrogenation if one will not perform a series of calibration runs. Due to surface states the curves do not give diffusivity, except in our case at temperatures too high for proper hydrogenation (3). The proper range for hydrogenation is 450-500°C for 3/8" rods.

High vacuum annealing treatments can be carried out up to 900°C in the vycor fire tube. Pressure step functions can be applied by changing the reservoir content of hydrogen between periods of contact with the rods. The manometer can be used to reduce the reservoir content in 1.4% steps by successive isolation and evacuation. The final pressure at equilibrium after each hydrogen admission to the rods gives a pressure-temperature-concentration equilibrium point for the columbium-hydrogen system.

One can use octoil or mercury in the manometer. Octoil gives 14 times the sensitivity of mercury. From experimental measurement the sorption of hydrogen by octoil is negligible. With the two manometer fluids the range of accurate pressure measurement is 7-990 mm Hg. The manometer consists of a uniform diameter, one meter long pyrex U-tube, which straddles a meter stick and is carefully mounted in a vertical position. A row of mirrors permits the elimination of parallax by merging

the meniscus with its image. Liquid air traps on either side of the manometer isolate the rods and the ion gage from mercury vapor in the manometer. A consolidated extended-range Phillips type of ionization guage reads vacuum pressures from 10^{-7} to ½ mm Hg dry-air-equivalent.

A Globar furnace with a West stepless controller holds the rods at a constant temperature. The rods are positioned so that the rod temperature is uniform to about one degree centigrade and the controller is able to reduce temperature drift to the same degree. System temperature is measured by three thermometers and the reservoir is wrapped in aluminum foil to prevent any greenhouse effect. A fan insures room circulation and turbulence to maintain a uniform room temperature. The laboratory is well inside a large building so that room temperature will vary no more than 2-3°C if precautions are taken regarding windows and doors in adjacent rooms. Fig. 3 is a block diagram of the system.

Accuracy and Uniformity

The volume calibration was carried out to about ¼%. With the accuracies of pressure and temperature the average hydrogen contents could be calculated to better than 1%. With not too high a hydrogenation temperature, macroscopic uniformity can be kept within a range of variation of 1%. Considerable attention to detail in design and procedure is required to achieve this accuracy.

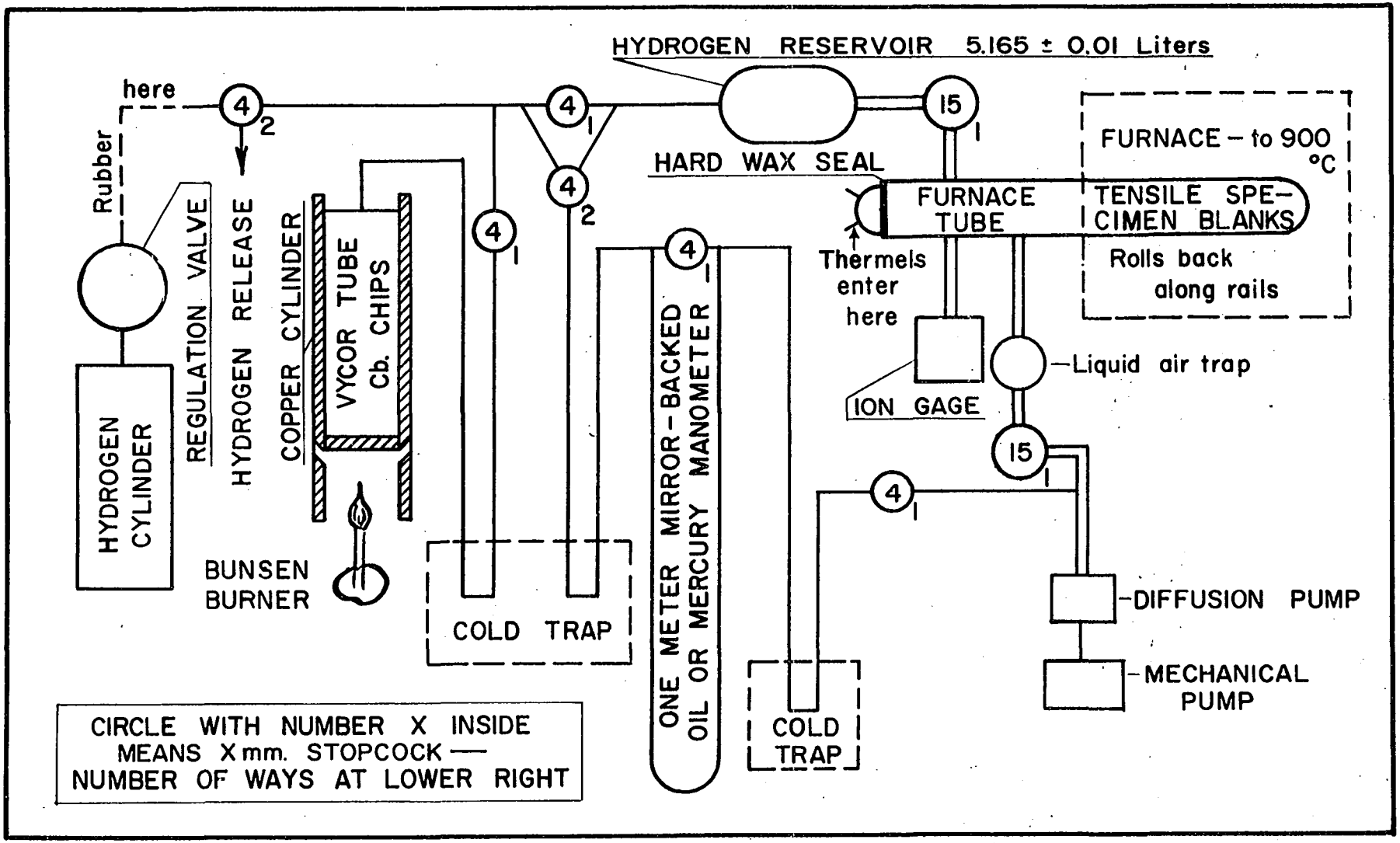


Figure 3 BLOCK DIAGRAM OF HYDROGENATION SYSTEM

To obtain accuracy of hydrogen content one must determine accurately the following quantities: Pressure, effective volume (which is a function of furnace temperature), and system or "room" temperature. Also the reservoir volume must be measured accurately. The system temperature, averaged over an interval of time at any point in the system (outside the hot zone), must be constant at the average of the thermometer readings. The fan effects this quite closely, as is seen from the minute relative variations between the thermometer readings.

Also, the furnace positioning and thermal insulation geometry must be reproducible from run to run. Time must be allowed for the detection of thermal disequilibrium and its disappearance. The manometer must be carefully read. The expansion on opening the reservoir to the system is very nearly free and hydrogen is more ideal at these pressures than is required.

From the ideal gas law and elementary considerations, one has the following formula for parts-per-million of hydrogen in the columbium:

$$\text{ppm} = 10^6 \, \bar{r} \; / \; (92.17 \neq \bar{r})$$

where $\bar{r}$ is the average number of hydrogen atoms in the columbium per atom of columbium, and:

$$\bar{r} = \frac{2 \, Ve \, m}{R \, M} \cdot \left(\frac{Pb \, Vb}{Ve \, Tsi} - \frac{Pf}{Tsf} \right)$$

where Ve is the effective volume at this furnace temperature, m is the atomic weight of columbium, M is the mass of columbium

being heated, R is the ideal gas constant, Pb is the pressure at equilibrium of hydrogen in the isolated reservoir initially, Vb is the reservoir volume, Pf is the final (constant) pressure, Tsi is the system temperature, or reservoir temperature to be slightly more accurate, at the beginning of the run, and Tsf is the system temperature at the end of the run, when the pressure has become constant.

The system must, and can reliably, be made very leak-tight for purity and accuracy. One must exercise reasonable care in procedure, especially in regard to the demountable seal. The after-run, overnight leak tests rarely showed a measurable pressure rise on the manometer, and the Phillips guage pressures rose a score or so microns, where the rise could be measured. With proper preparation a vacuum system will hold a vacuum indefinitely.

Uniformity is attained by proper positioning of the rod bundle along the horizontal fire tube. There is a maximum in the temperature profile along the firetube, and thermal inhomogeneities will be minimized with rod bundle placement at this point. Chromel-alumel thermocouples were placed variously at each end of the rod bundle. Their readings were kept no more than a few degrees C apart. The junctions were not welded nor usually in direct contact with the rods so that the temperature change along or across the bundle was a minor fraction of the thermocouple difference, due to the existence of the boundary layer in the hydrogen and the high thermal conductivity of columbium.

Using the thermocouple difference as a high upper bound to nonuniformity one can obtain the formula:

$$dr/r = dC/C = (1/r) \cdot (\partial r/\partial T)_p \cdot (1\ dT/L)$$

where C is hydrogen concentration, r is the aforementioned atomic ratio, T is temperature, l is the gage length of the tensile specimens, L is the length of the rods, and dT is the thermocouple reading difference. It is assumed that a small temperature gradient has insignificant effect on the solubility of the hydrogen in the columbium. One can make a plot from equilibrium data giving the high-upper-bound nonuniformity of the hydrogen content for various run conditions (30,32). The nonuniformity was less than 2% for our runs.

The quench-enrichment or radial nonuniformity can be rendered negligible by hydrogenation temperatures (for our apparatus and 3/8" rod) of 450-500°C. Somewhat higher temperatures will result in a crudely estimable radial nonuniformity. The diffusion problem here is extremely difficult, but a crude overestimate can be made and the nonuniformity can be taken as half this with uncertainty limits of equal magnitude.

One method of estimating this radial nonuniformity is to obtain a Dt/a^2 value from the time length of quench pickup and therefrom a ratio of gage radius concentration to the (assumed constant) surface concentration. This ratio was multiplied by the surface concentration. The surface concentration was taken as twice the increase in average

concentration on quenching. This estimate is apparently too high due to the exothermic nature of the Cb-H system but a retarding surface state will be present. This estimate is order-of-magnitude only and useful only below the temperatures where the quench enrichment becomes significantly large. Quench enrichment data does exist for the second heat, however. For diffusion calculations see reference 33.

Nonuniform hydrogen distributions may be desired, but control over these is insufficient unless calibration runs are taken. Due to the higher-than-average maximum hydrogen concentration and internal stresses consequent to nonuniform hydrogen distributions, nonuniform hydrogen distributions are equivalent to somewhat more concentrated uniform distributions. Since in practice hydrogen distributions will be often nonuniform, for practical significance of one's data one should study some nonuniform hydrogen distributions. On the other hand a uniform distribution of hydrogen is easier to understand theoretically. However some data on nonuniform distributions was taken using the material of the first heat.

Purity

The purity of the hydrogen atmosphere, which is important to the surface condition of the rods during hydrogenation and to any high-temperature hydrogenation treatments in regard to mechanical properties, depends on the following factors: The efficiency of the chips as a purification train, the leak-

tightness of the system, and the amount of residual outgassing after the commencement of the run.

The principle behind using columbium chips as a purification train is as follows. Gases in general have either a considerably more or considerably less energetic reaction with columbium than has hydrogen. Hydrogen is anamolous in this respect. Thus when hydrogen is sorbed into the columbium chips the impurity gases which are more strongly reactive are permanently bound, whereas those gases which react weakly or not at all are removed on evacuation when the chips are cooled. Sacrifice of the first hydrogen to evolve on reheating furthers purification as does passing the gas through a long liquid air trap. Cb_2O_5 powder (yellow when stoichiometric and dangerous) should be avoided as reduction can give 1/3% H_2O in the hydrogen atmosphere (2,19). However no yellow powder was ever observed on examination of the used chips.

With care in procedure leak-tightness was no problem. The leak-rate upper bound can be estimated by the ion guage reading before the run after the two to three day pumpdown. Part or all of this gas is outgassing. The overnight leak tests indicate likewise that with care the leak rate is negligible. Diffusion of air into the system and of hydogen out of the system is appreciable only near the 900°C temperature limit of the firetube.

Outgassing is the largest source of impurity gas. It has many sources: The glass walls of the system, stopcock grease, the subsurface of the glass walls and the metal

surface (cleanliness) in the firetube, absorption on the chip surfaces, desorption of air from the manometer fluid, outgassing from the components of the Phillips guage, any dirt introduced with the rods, etc.

Thermal equilibration or vacuum annealing before the run eliminates the fire-tube-and-rods outgassing source which is the largest. This procedure is a partial bakeout. To utilize the advantage of ultra-high-vacuum technique the other impurity sources (chips, manometer, etc.) must be correspondingly reduced. The partial pressure of impurity gas rises during the run and attains a plateau during the overnight leak test. Its magnitude is variable and only crudely measurable with our rather simple equipment, but is a few to a few dozen microns Hg. The color of the Phillips guage discharge is some indication of the purity of the residual gas-hydrogen atmosphere. Test runs have been taken to measure residual gas accumulation under various conditions imposed on the system. Due to continual gettering by the hot rods of the oxygen and (more slowly) nitrogen impurities the impurity pressures over the hot rods are much less than in the absence of the rods. The impurity pressures generated with a cold fire tube are small compared to those in the case of an insufficiently baked fire tube. Even with our worst impurity pressures (70 microns Hg or so) bright annealing of the columbium has always been the case. See Appendix C, reference 30 for a detailed treatment of hydrogenation.

Post-Hydrogenation Considerations

Certain post-hydrogenation procedures and "effects" influence the hydrogen distribution in the columbium samples. These are hydrogenation and dehydrogenation from the nominal 3/8 micron of hydrogen in the atmosphere, contamination of the surface of the machined tensile specimen, and diffusion of quench-enrichment hydrogen from the rod circumference and ends into the gage section (34).

From diffusion and contamination hardening data (16), it may be concluded that contamination hardening (oxygen being the predominant hardener) is negligible except for prlonged high-temperature treatments. However, from the diffusivity of hydrogen in columbium (3) and equilibrium data and the nominal hydrogen content of the air (34) considerable change in hydrogen content should have taken place during high temperature testing and/or remaining some months in air at room temperature. Consequently dehydrogenations of the specimens broken in high temperature tensile tests and (independently) in other tests were performed after 130 days. From equilibrium data and the amount of hydrogen in the gas phase, the original hydrogen content before dehydrogenation was determined. (See Appendix B, reference 30.) There was no measurable change. The implication of this result is that a surface stage in the sorption-desorption reaction chain had become controlling with a very low rate. Such a surface state would be expected from the Sievert's law behavior of

the Cb-H system away from the miscibility gap. In general, hydrogen can enter metals only as atoms.

Since the free energy of formation of atomic hydrogen is 48 kilocalories per mole (35), and since the hydrogen atoms must excite to outer adsorption sites on the Cb surface for recombination and evaporation, one would expect this state to "take over" and cut off hydrogen sorption and desorption below some temperature. From a simple Ahrennius treatment equating inflow and outflow the activation energy for desorption is larger than that for dissociation; thus below the "cutoff" temperature both of these processes will exhibit activation energies of 50,000 cal/mole or more.

Quench enrichment of the rod surface will not reach the gage sections in appreciable quantity if the machining of the rods is done within two weeks. Due to greater distance, the quench-enrichment at the rod ends is of no significance.

This account of the hydrogenation system and its operation is indicative rather than exhaustive and some study of vacuum physics and reference 30 should be made if a similar hydrogenation procedure is desired. References 33 and 36 are helpful. Reference 37 will be a useful starting point if one wishes to explore the application of ultra high vacuum technique.

CHAPTER V

DATA AND RESULTS

Data were obtained on three heats of columbium which had been refined by vacuum melting. The history and analysis of the third heat used is given in Table I. In the pages following only a fraction of the data will be given in the

TABLE I

ANALYSIS OF DU PONT HEAT D-1190

Element	Content in ppm by Weight
Oxygen	206
Nitrogen	50 or less
Carbon	50
Iron	122
Nickel	75
Chromium	10 or less
Copper	10 or less

Approximate History of du Pont Heat D-1190
1) Extruded warm from 3" round to 3/4" round.
2) Swaged from 3/4" round to 3/8" round at room temperature.
3) Part of material recrystallized and the remainder stress relieved.
4) Hydrogenated near 500°C for about one day.

interest of brevity. The effects of hydrogen content, strain rate and temperature on the yield strength, percent reduction

of area and fracture stress will be related in some detail. Then the remaining data will be summarized and interesting phenomena observed will be described. The full data is contained in reference 30.

History and Analysis of the Columbium Used

The third heat of columbium used was obtained from the du Pont Company as heat D-1190.

The recrystallization treatment consisted of a half hour anneal at 1200°C in high vacuum. The resultant grain structure was approximately equiaxed with a grain size of ASTM 6-7. The stress relief treatment consisted of an anneal of an hour at 825°C in high vacuum. The fine, highly elongated grain structure produced by the swaging treatment was not changed. While it is difficult to estimate a grain size for this kind of structure, and the grain size given will be of limited significance, it can be said that the original grain size before swaging was of the order of 10 microns.

Each heat of columbium is in a sense a different metal, since the properties of a metal depend on its analysis and history, and these factors differ from lot to lot. Since 700 ppm of oxygen doubles the proportional limit of columbium (38), and since the oxygen content of the electron beam melted columbium varies from about 100 to 300 ppm by weight, one can then expect a 15% variation from lot to lot in strength from this source alone. Thus if one is to evaluate the effect of one factor on the strength and other

characteristics of columbium, one must perform complete testing programs within individual lots of given history and analysis, as has been the procedure in this investigation.

The behavior of columbium in regard to ductility and other properties as well as strength can be affected by variations in history and anslysis. The recrystallized material of the third heat exhibited no ductility minimum, whereas the stress relieved material of the third heat exhibited a pronounced ductility minimum at hydrogen contents below 70 ppm by weight. The practical significance of the results lies mainly in that, in the absence of a ductility minimum, a few ppm of hydrogen are sufficient to effect a severe embrittlement at low temperatures.

Yield Strength Data

The yield strength is the most important strength quantity from a practical viewpoint as in the design of a part the calculated stresses must be limited below a safe fraction of the lowest stress producing measurable permanent deformation. In this section yield strength data for the stress relieved and recrystallized material of the third heat will be presented.

The yield strength of the stress relieved material of the third heat is presented as a function of hydrogen content, strain rate and temperature in Figures 4 and 5. In view of the two dimensional nature of a graph the strain rate is indicated by the symbol chosen for the data point according to Table II.

TABLE II

DATA POINT SYMBOLS FOR THE VARIOUS STRAIN RATES

Symbol	Strain Rate
Semicircle	2.0 ipm/.815"
Triangle	0.20 ipm/.815"
Dot	0.020 ipm/.815"
Circle	0.0020 ipm/.815"

The strain rate is given in the conventional manner, the speed in inches per minute of the Instron machine crosshead being symbolically divided by the gage length of the tensile specimen employed. The crosshead speed of the machine is constant; a simple formula gives the true strain rate until maximum load, where necking begins (30).

The plots of yield strength data in Figures 4 and 5 show that hydrogen has little effect on the yield strength of columbium at room or at elevated temperatures. There may indeed be a slight weakening resultant from large hydrogen contents; but the trend is not large relative to scatter and no definite conclusion can be drawn. At low temperatures there is a moderate strengthening. At liquid air temperatures there is a solid solution strengthening which attains a maximum magnitude of 15% at a hydrogen concentration of 50-75 ppm by weight. The strengthening observed at -77°C is lesser in magnitude.

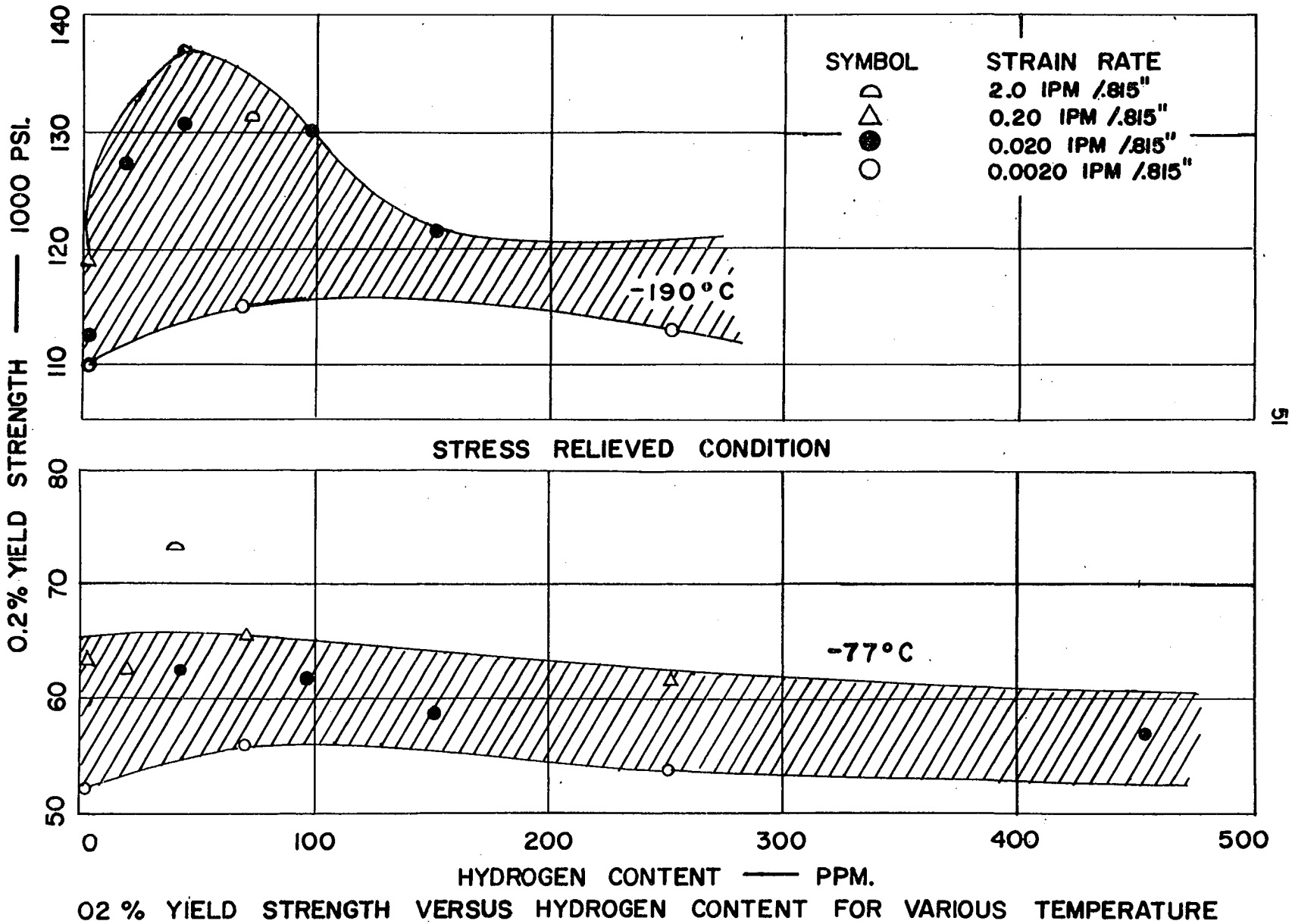


FIGURE 4

02 % YIELD STRENGTH VERSUS HYDROGEN CONTENT FOR VARIOUS TEMPERATURE

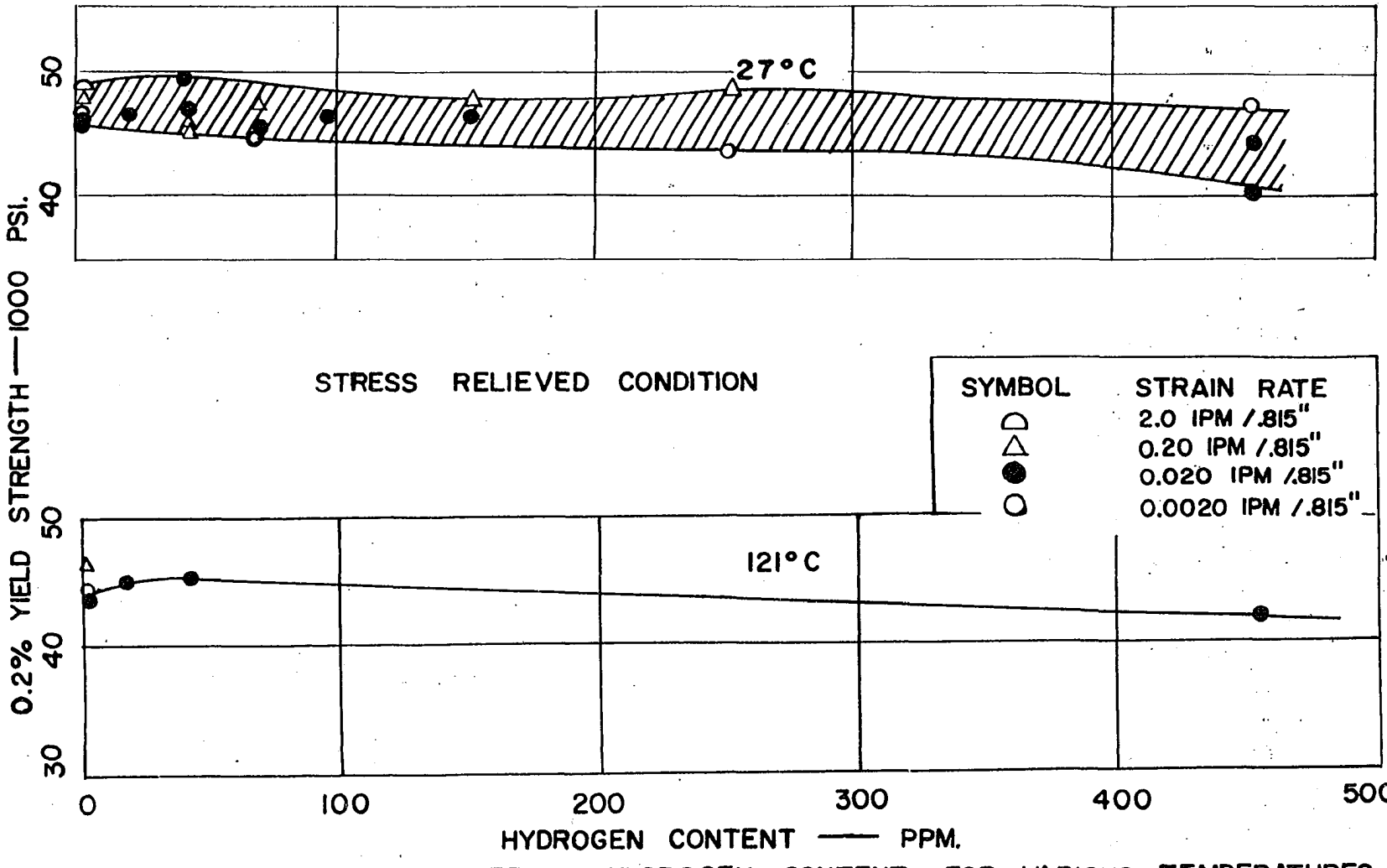


FIGURE 5

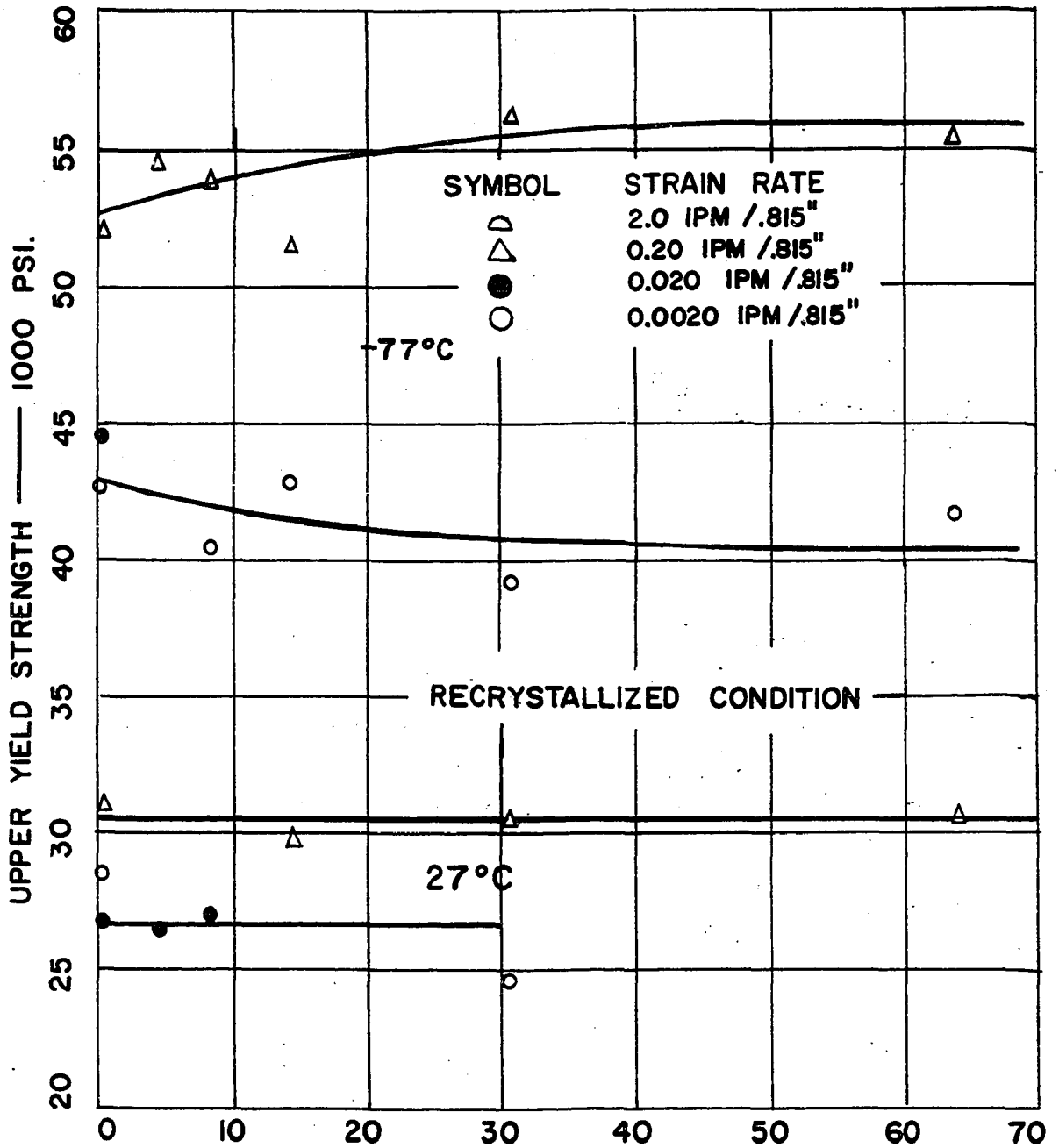
02% YIELD STRENGTH VERSUS HYDROGEN CONTENT FOR VARIOUS TEMPERATURES

The yield strength data for the recrystallized material of the third heat is plotted in Figures 6 and 7 against hydrogen content for various temperatures. The strain rate is given by the point symbol as in Table II. One observes a larger relative strain rate dependence of the yield strength for the recrystallized material than for the stress relieved material. At -190°C there is also in the case of the recrystallized material a solid solution strengthening of the same relative magnitude as that for the stress relieved material. At ambient and elevated temperatures there is, as in the case of the stress relieved material, no determinable dependence of the yield strength on hydrogen content. The large strain rate dependence of the yield strength at -77°C for the recrystallized material is discussed later.

Percent Reduction of Area Data

The data of percent reduction of area at fracture for the third heat stress relieved material is presented in Figures 8 and 9 and plotted against hydrogen content for various temperatures. Figure 10 is a similar plot presenting the per cent reduction of area data for the recrystallized material of the third heat. Figure 11 is a plot versus temperature of the reduction of area data contained in Figures 8, 9 and 10. The hydrogen content is given by the symbol used for the point according to the table in the figure.

The percent reduction of area of the stress relieved material of the third heat is observed from Figures 8 and 9 to decrease with increasing hydrogen content at any given temperature. The decline is most precipitous at about -77°C, although the decline is considerably more rapid at -190°C



UPPER YIELD STRENGTH VERSUS HYDROGEN CONTENT FOR VARIOUS TEMPERATURES

FIGURE 6

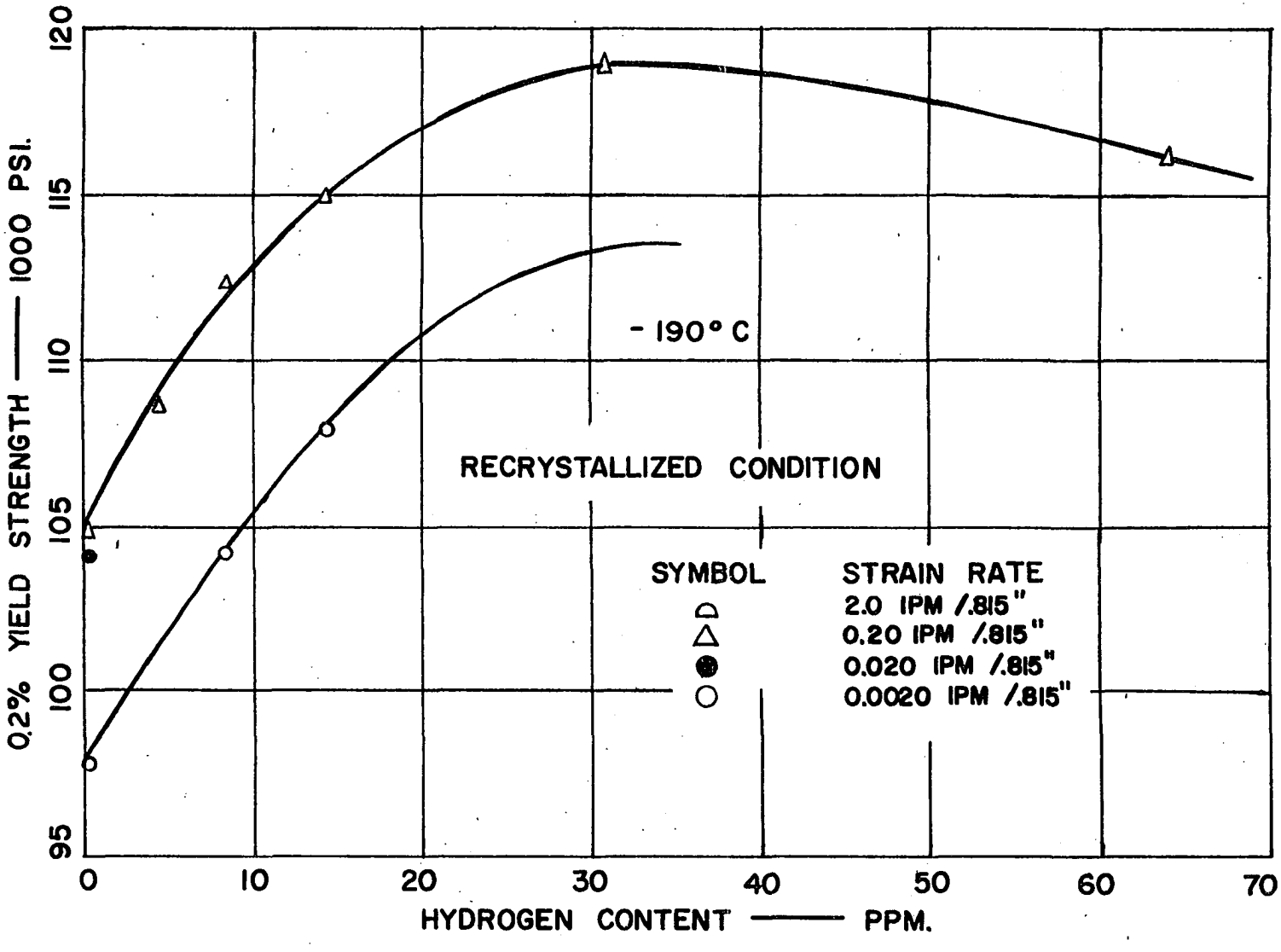


FIGURE 7

0.2% YIELD STRENGTH VERSUS HYDROGEN CONTENT FOR VARIOUS TEMPERATURES

than at ambient temperatures. From Figure 10 it is observed that the recrystallized material of the third heat behaves in the same way, although the ductility data obtained from this material was poor for hydrogen contents between zero and ten ppm by weight. A plot of mechanical property data against specimen number, the specimens being numbered consecutively from one end of the rod, indicated a contamination or inhomogeneity of the end of the rod from which most of the relevant material was taken.

The absence of the ductility minimum in the material of the third heat that was recrystallized is exhibited in Figure 11. The percent reduction of area of the stress relieved material dropped to low values when temperature was decreased to -77°C; but on further decrease in temperature to -190°C, for hydrogen contents of 20-40 ppm the percent reduction of area climbed above 50%.

Fracture Stress Data

The data of fracture stress for the third heat stress relieved material is presented in Figure 12, 13, 14, 15, and 16. From Figure 12 one concludes that at 120°C hydrogen contents larger than 400 ppm are required to greatly reduce the fracture stress of columbium. Figure 13 shows that at ambient temperature the fracture stress of columbium is decreased significantly by hydrogen contents in excess of 50 ppm. The data presented in Figure 14 demonstrates that at -77°C hydrogen contents lower than 20 ppm reduce fracture stress to a minor fraction of the fracture stress of pure columbium. At -190°C, as is shown by the data of Figure 15, the decrease of fracture stress with increasing hydrogen content is less

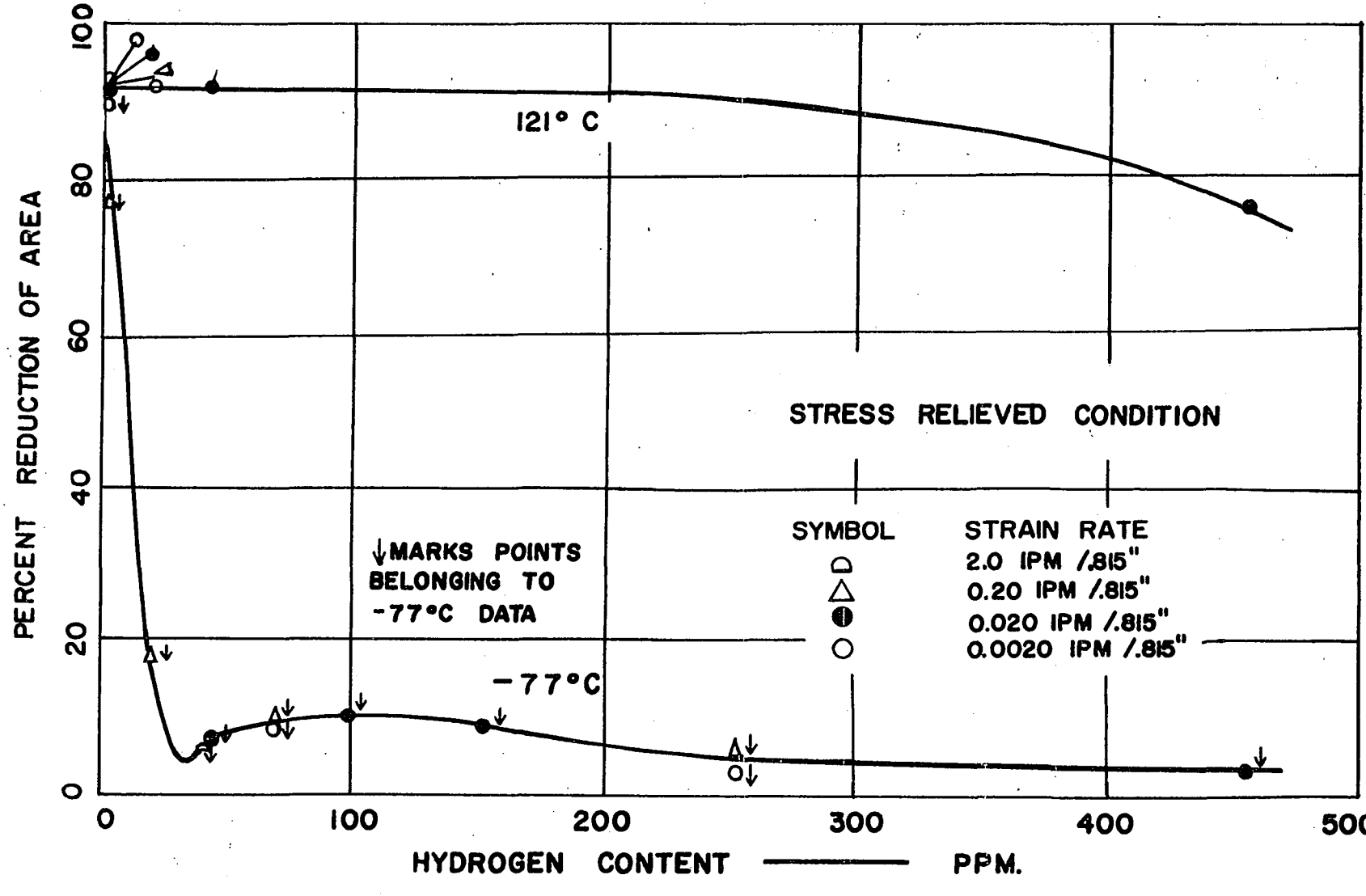


FIGURE 8 — REDUCTION OF AREA VERSUS HYDROGEN CONTENT FOR VARIOUS TEMPERATURES

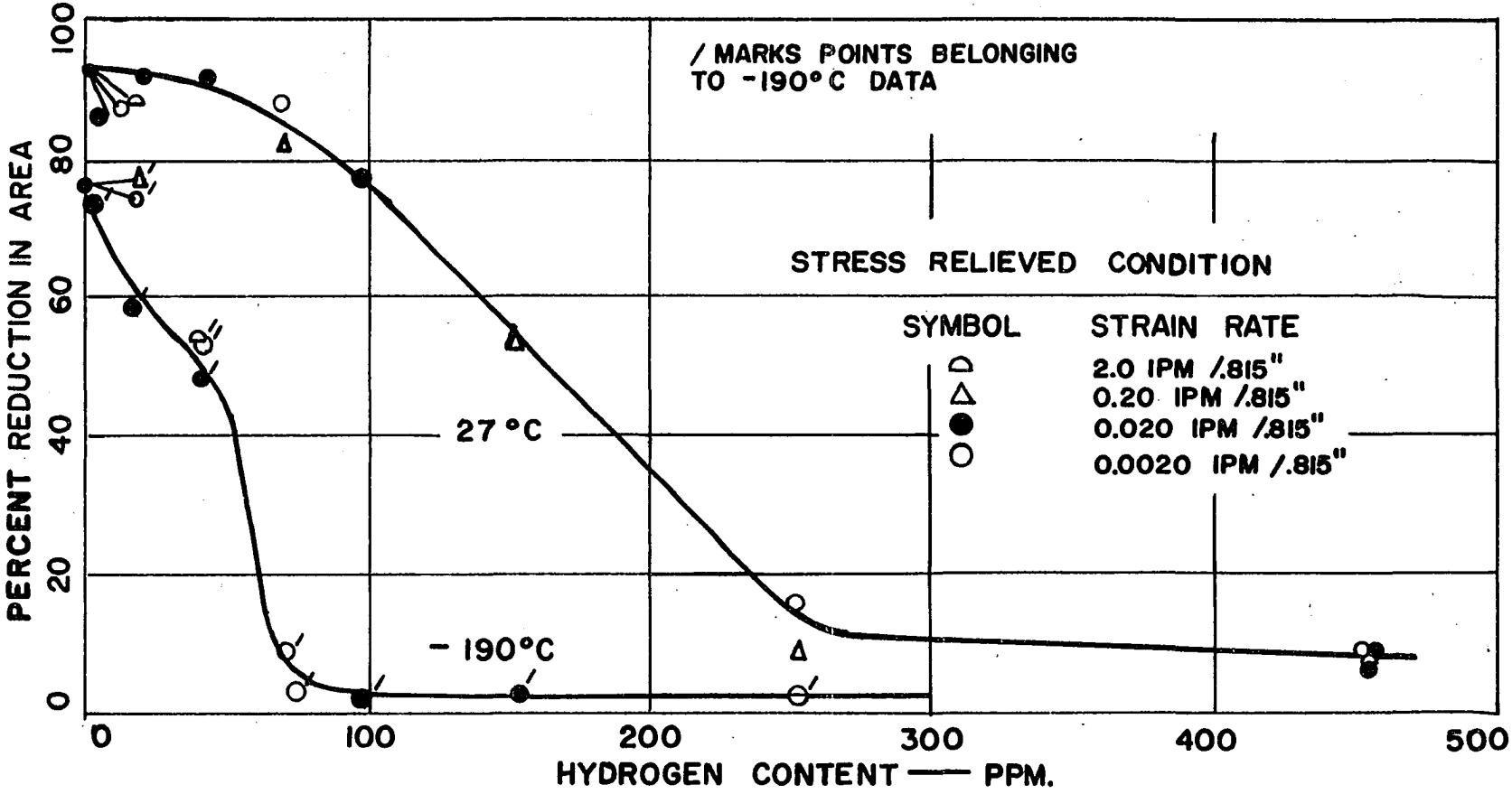
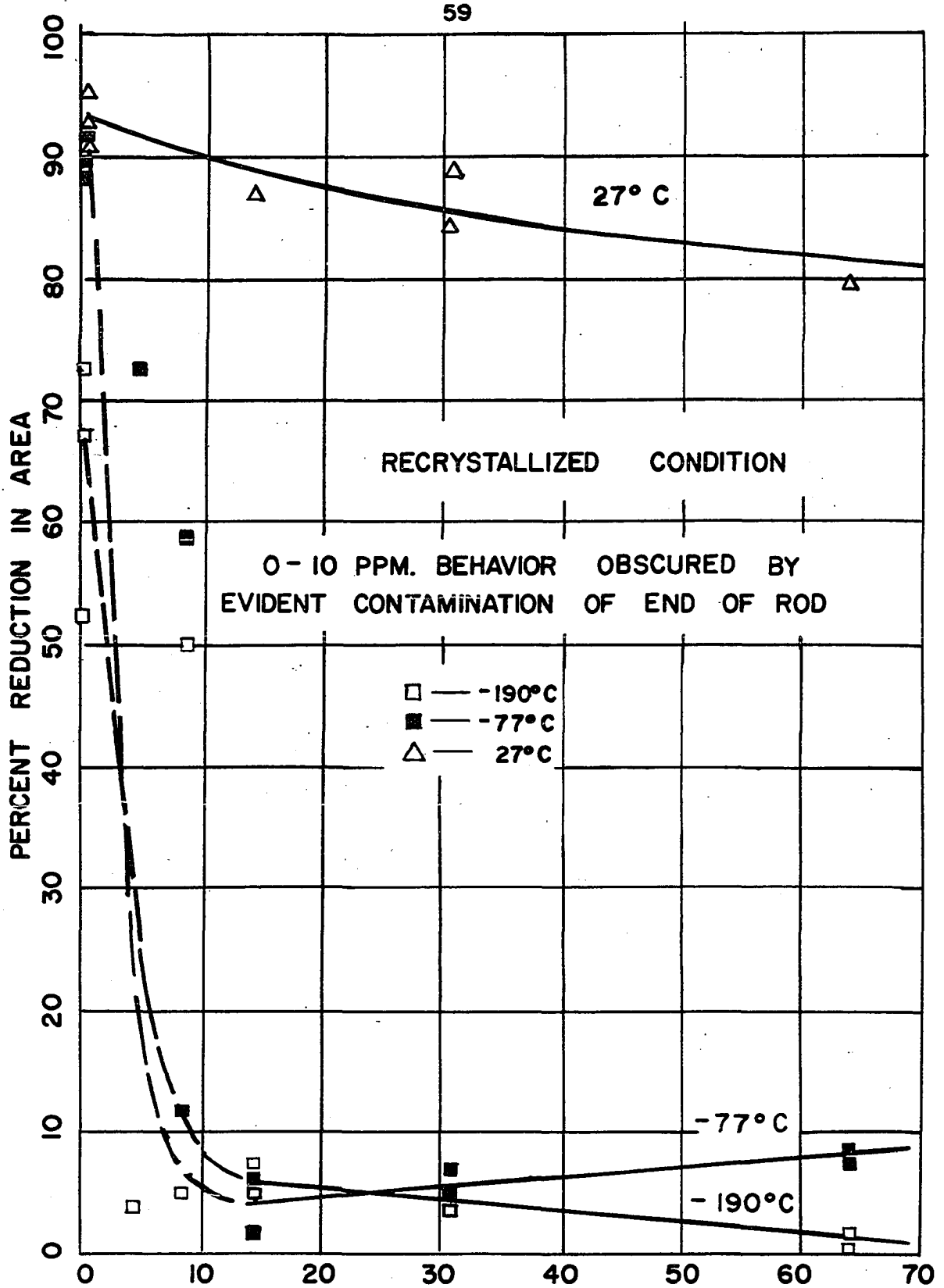


FIGURE 9 REDUCTION OF AREA VERSUS HYDROGEN CONTENT FOR VARIOUS TEMPERATURES



REDUCTION OF AREA VERSUS HYDROGEN CONTENT FOR VARIOUS TEMPERATURES

FIGURE 10

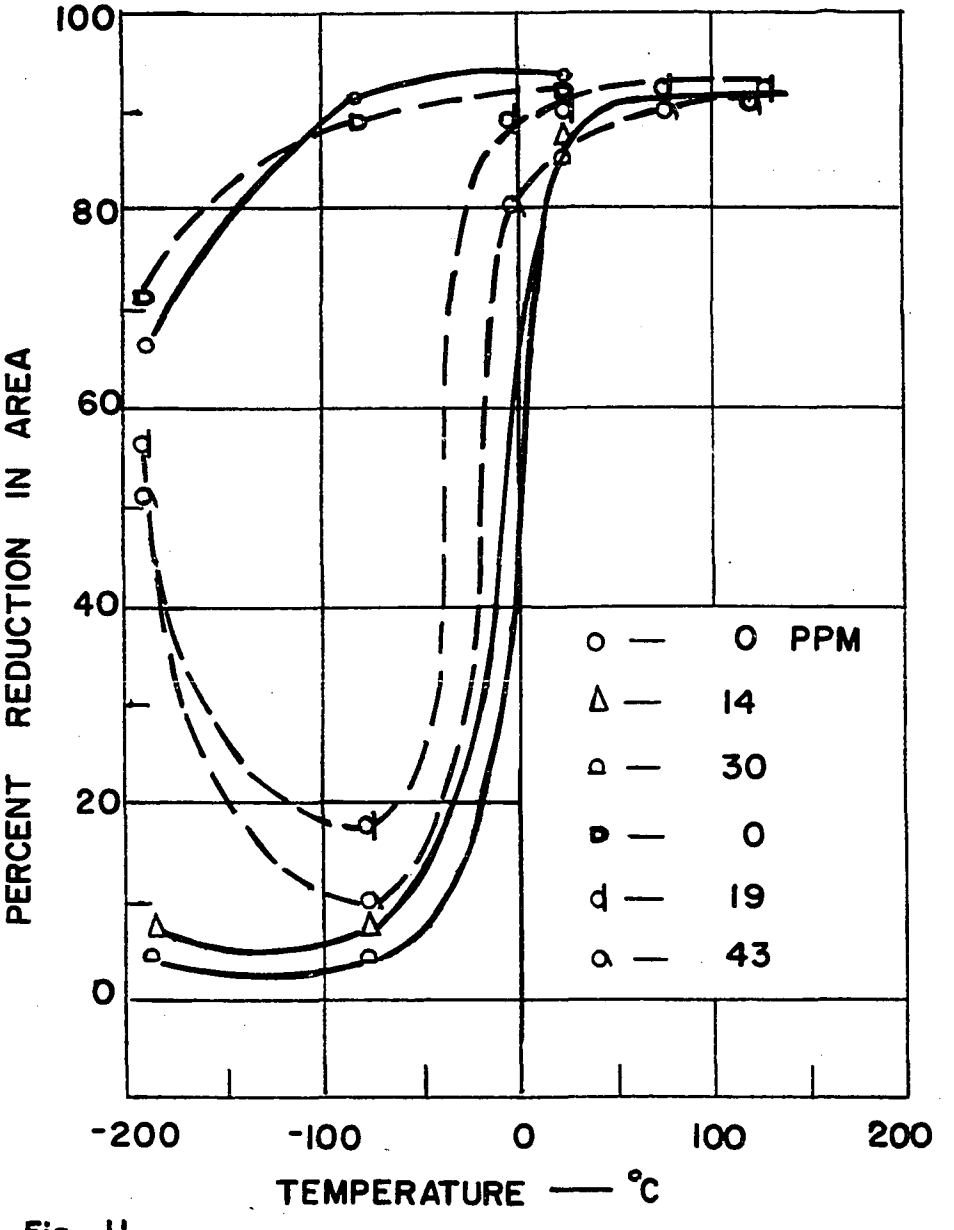


Fig. 11.
COMPARATIVE DUCTILITY OF STRESS RELIEVED AND RECRYSTALLIZED SAMPLES OF COLUMBIUM-HYDROGEN ALLOYS.

STRESS RELIEVED - - - - -
RECRYSTALLIZED ———

rapid than at -77°C. The fracture stress has been only halved by hydrogenation to a hydrogen content of 70 ppm. Figure 16 is a plot of data in Figures 12, 13, 14, and 15 exhibiting the dependence of fracture stress on temperature for various hydrogen contents. One observes a pronounced minimum in fracture stress near -100°C, except for in the pure columbium.

The data of fracture stress for the recrystallized material of the third heat is presented in Figures 17, 18, 19, and 20. The fracture stress behavior of the recrystallized material is seen to be similar to the behavior of the stress relieved material. The fracture stress of the recrystallized material is seen, however, to be lower than the fracture stress of the stress relieved material. This difference is evidently due to the considerably larger mean grain diameter of the recrystallized material in the direction of maximum resolved shear stress. This circumstance will permit larger dislocation pileups and resultant microcracks in the recrystallized material than in the stress relieved material.

Data of First and Second Heats

Similar testing conditions produced similar results for all of the material used. The first heat consisted of 35 specimens and was used for a preliminary survey of the mechanical properties of columbium. Data were obtained for the as-received state, and for various thermal treatments of the columbium. One hydrogenation was performed to determine the hydrogen concentrations to be investigated subsequently.

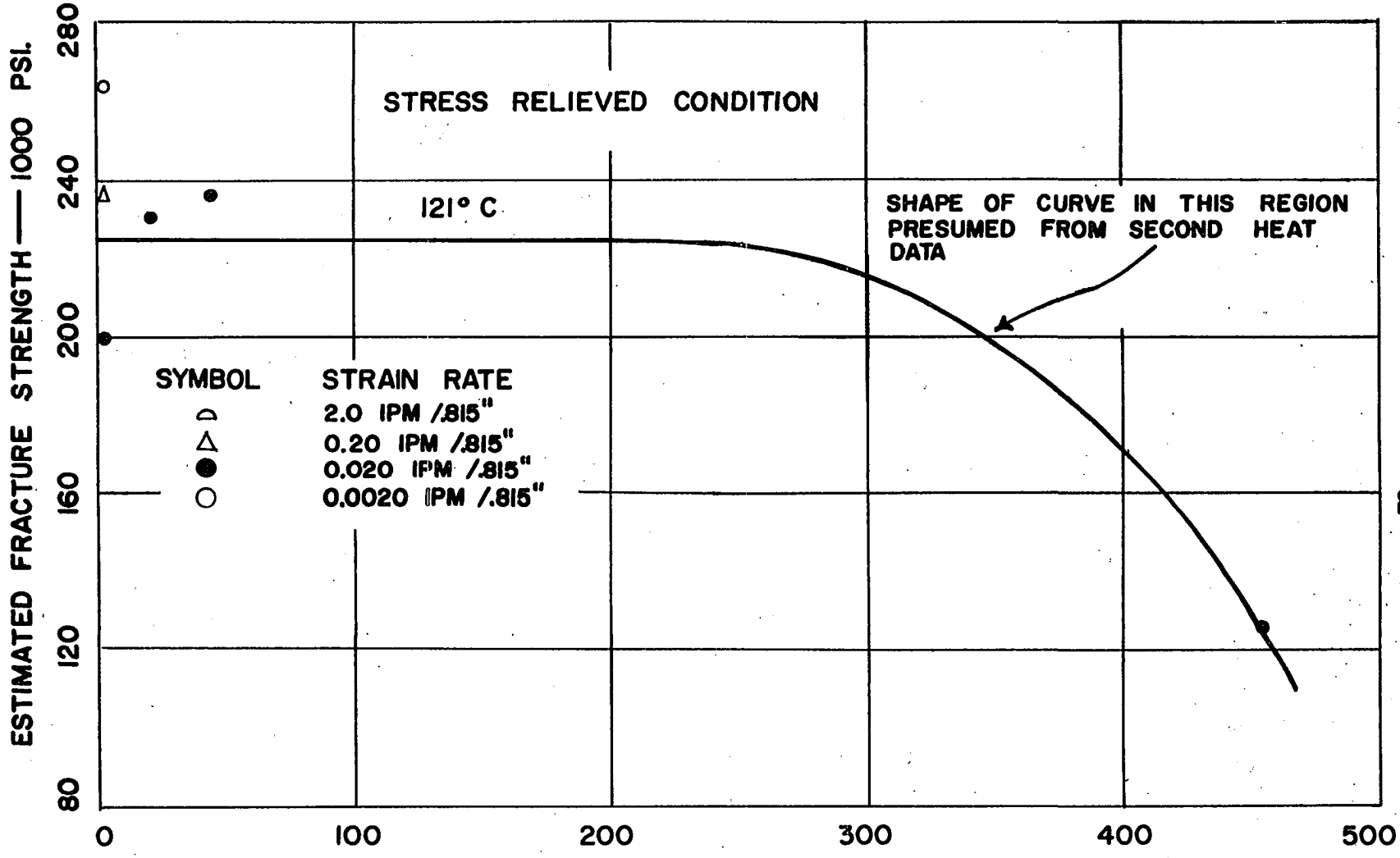


FIGURE 12

ESTIMATED FRACTURE STRENGTH VERSUS HYDROGEN CONTENT FOR VARIOUS TEMPERATURES

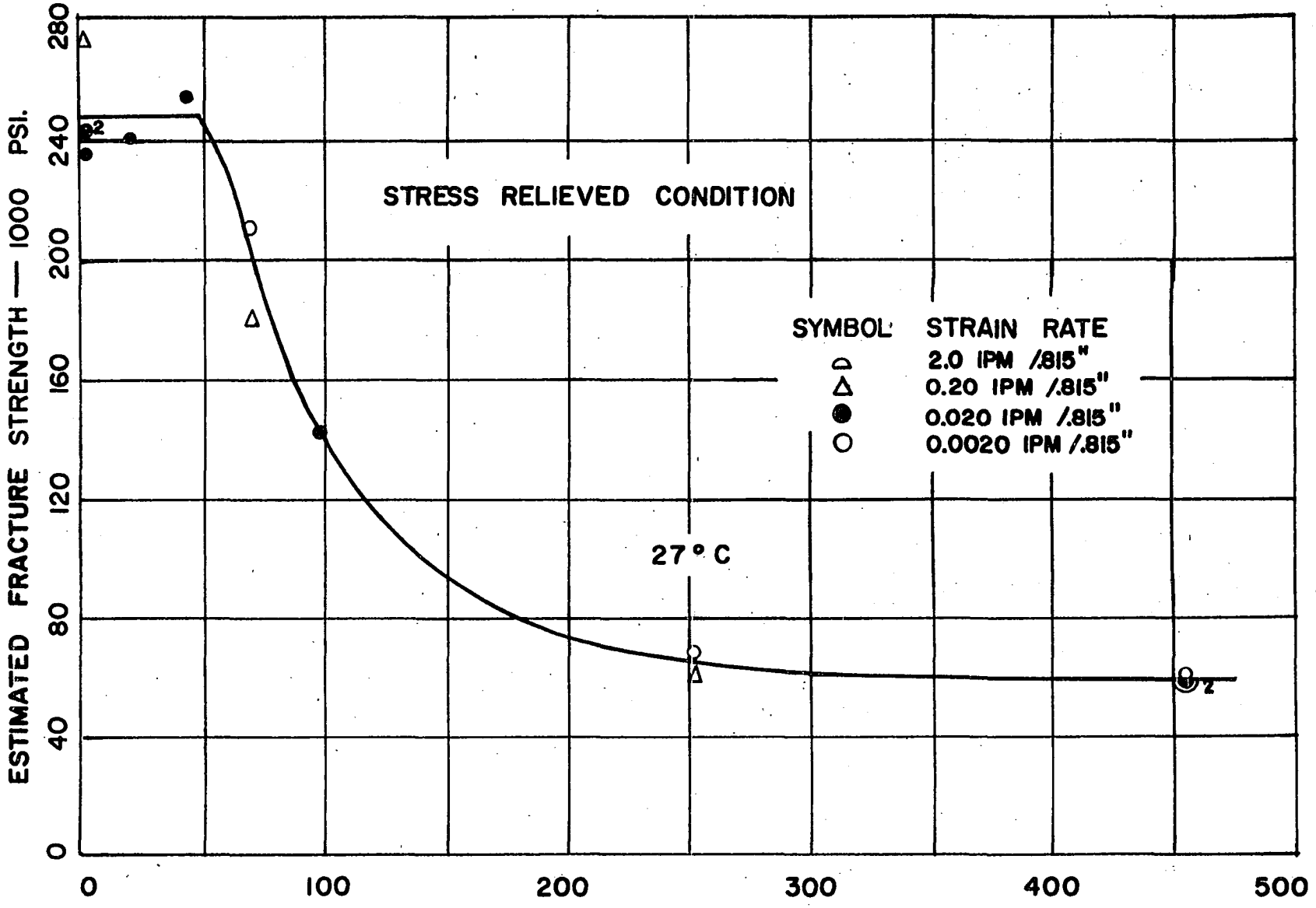


FIGURE 13

ESTIMATED FRACTURE STRENGTH VERSUS HYDROGEN CONTENT FOR VARIOUS TEMPERATURES

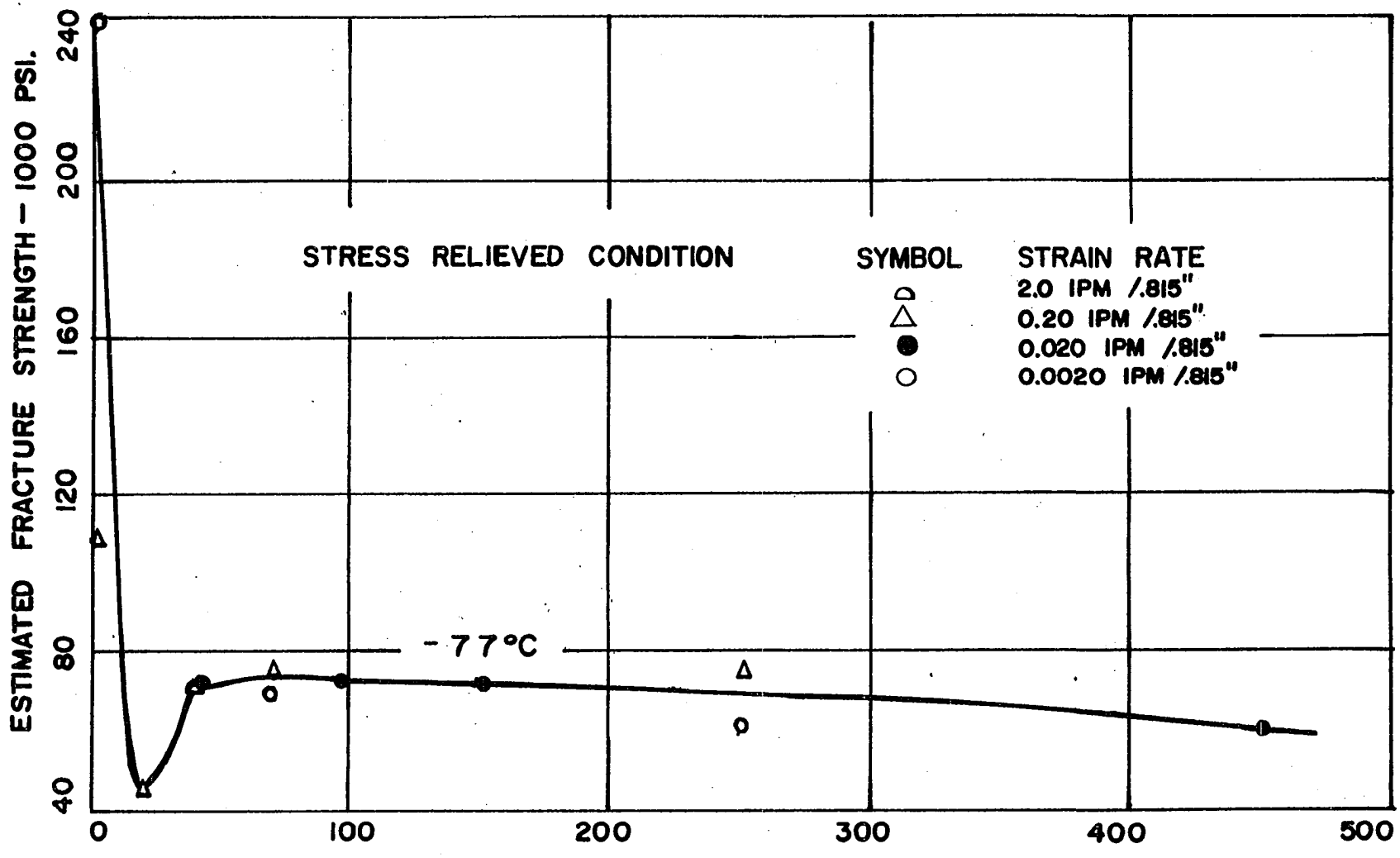


FIGURE 14

ESTIMATED FRACTURE STRENGTH VERSUS HYDROGEN CONTENT FOR VARIOUS TEMPERATURES

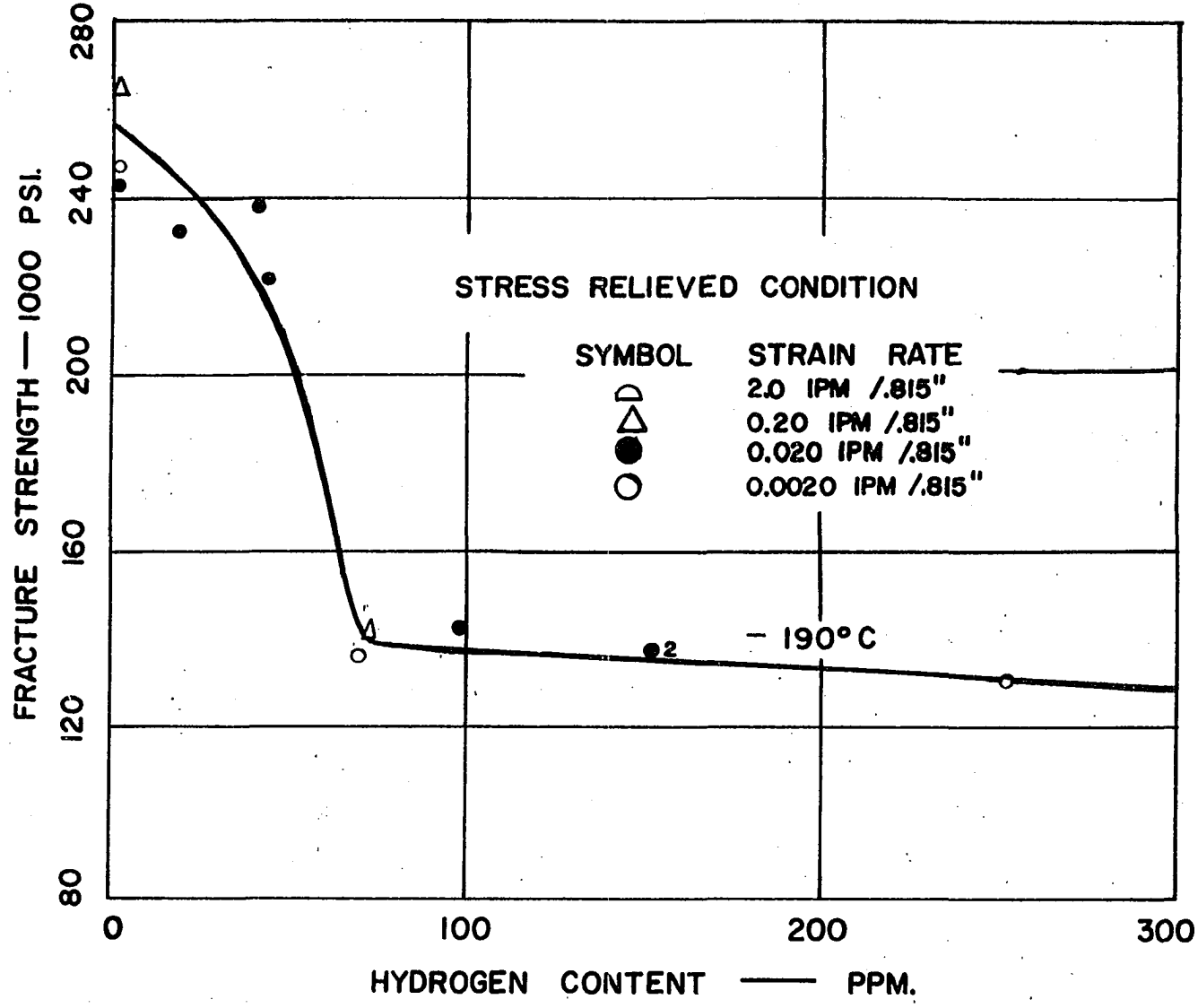


FIGURE 15

ESTIMATED FRACTURE STRENGTH VERSUS HYDROGEN CONTENT FOR VARIOUS TEMPERATURES

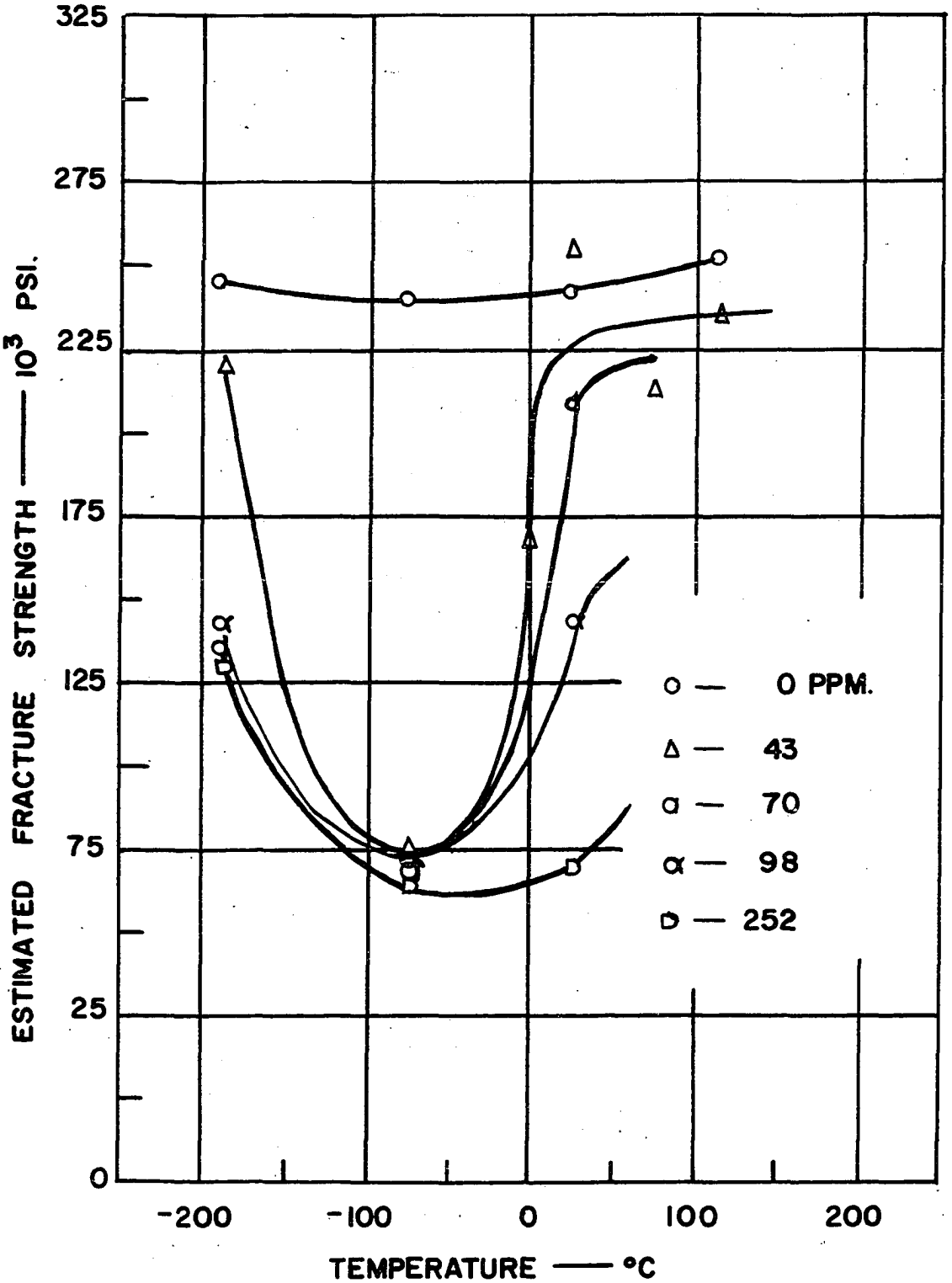


FIG. 16
FRACTURE STRESS VS. TEMPERATURE, STRESS RELIEVED COLUMBIUM-HYDROGEN ALLOYS.

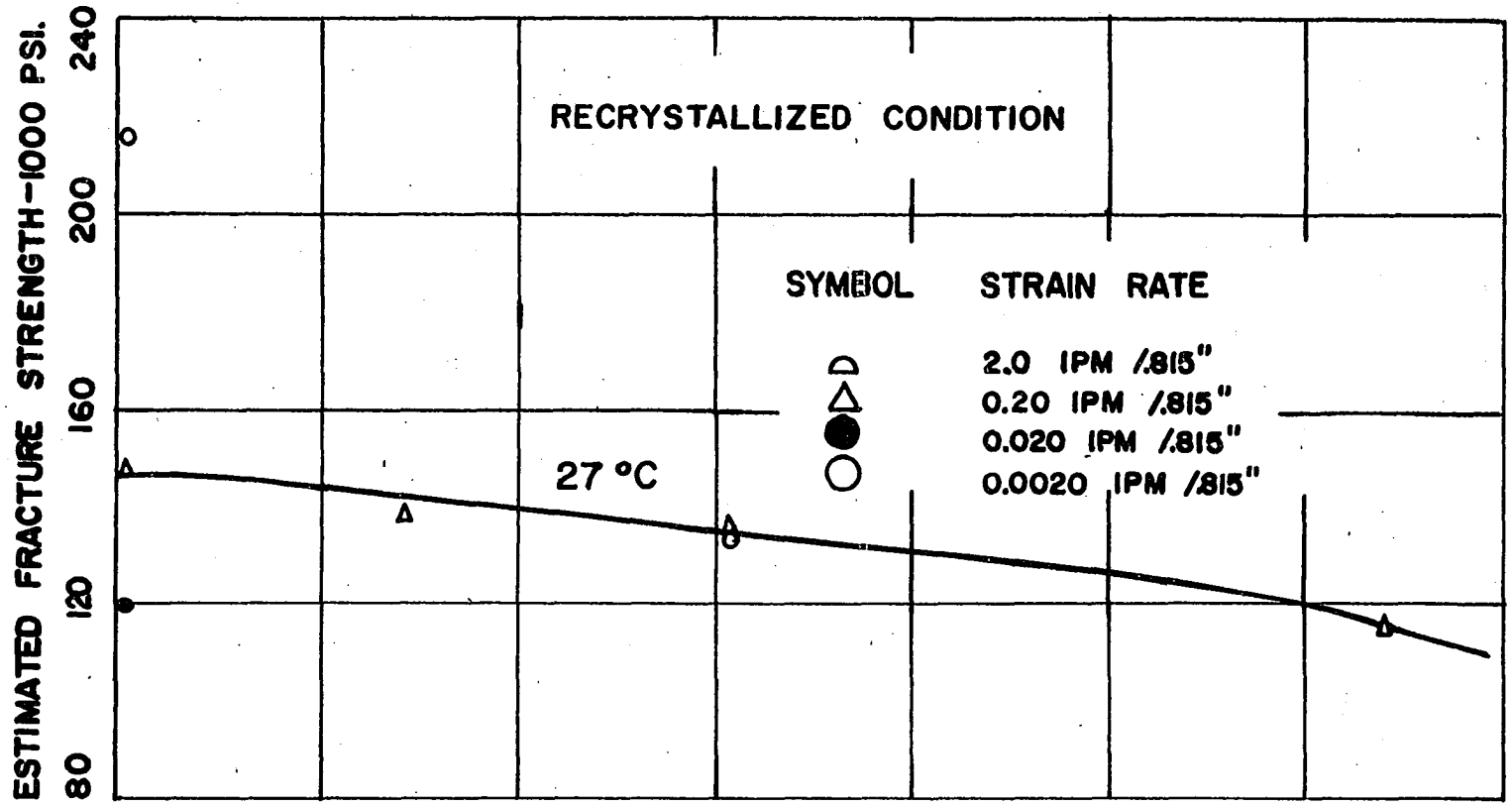


FIGURE 17

ESTIMATED FRACTURE STRENGTH VERSES HYDROGEN CONTENT FOR VARIOUS TEMPERATURES

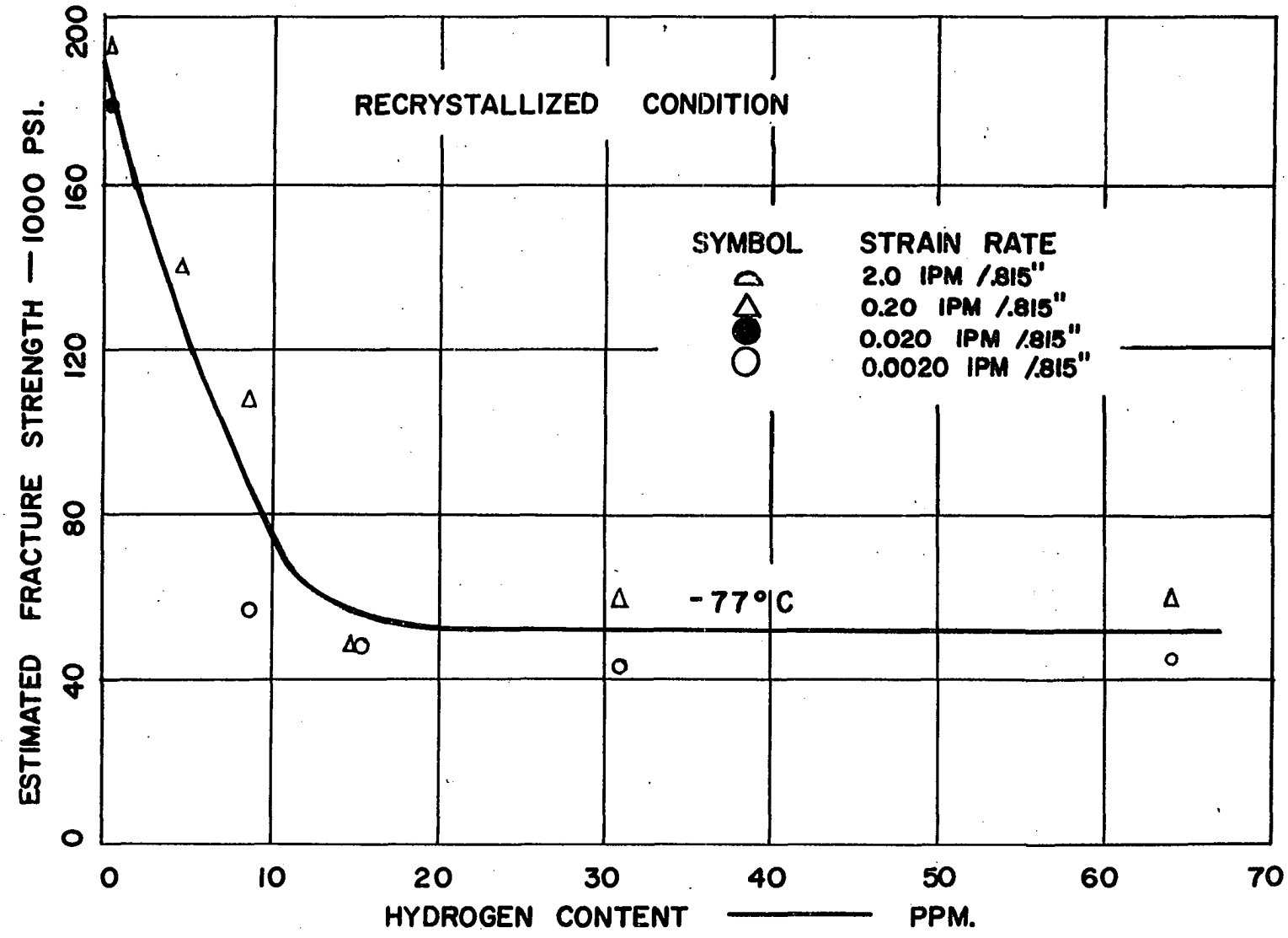


FIGURE 18

ESTIMATED FRACTURE STRENGTH VERSUS HYDROGEN CONTENT FOR VARIOUS TEMPERATURES

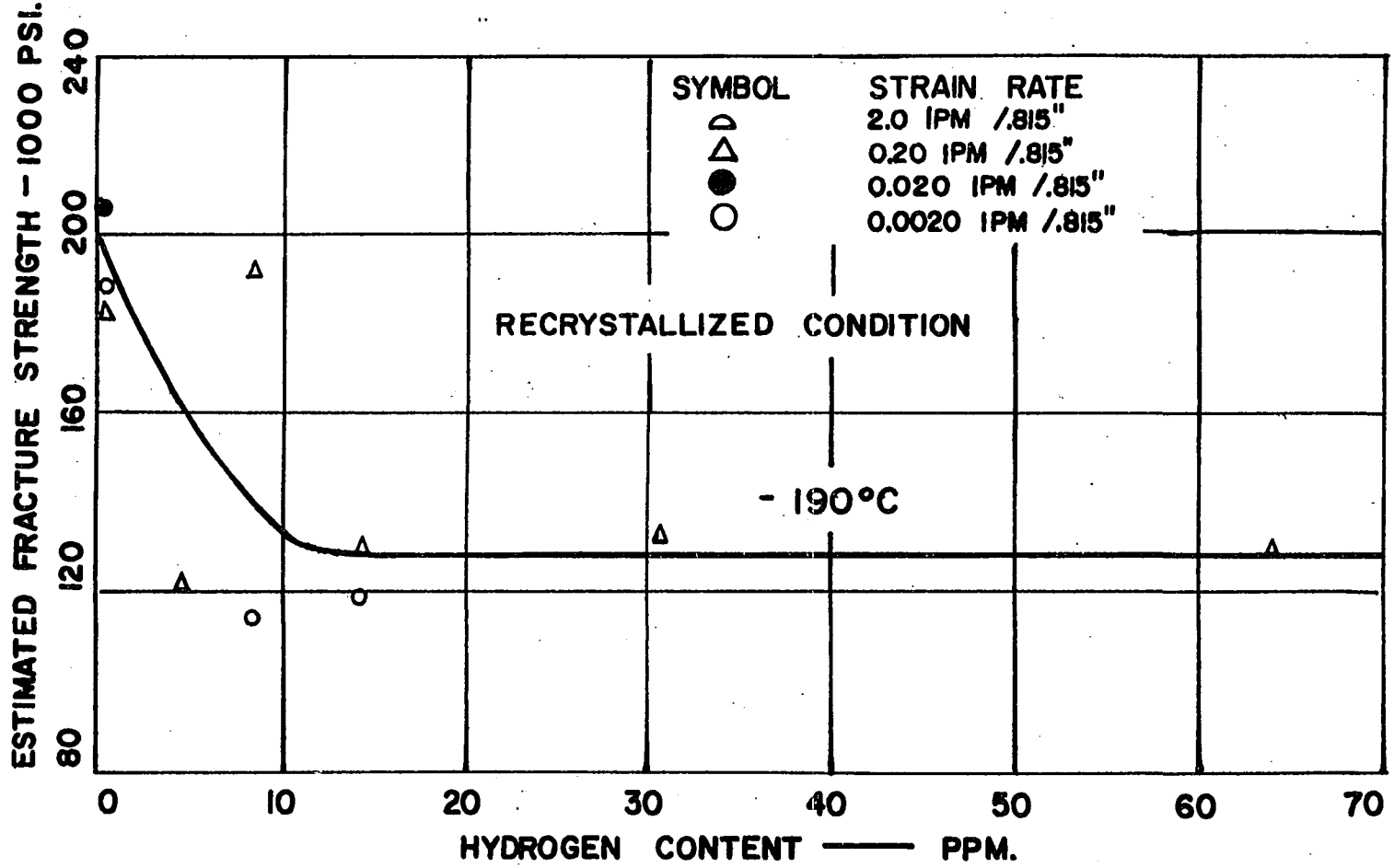


FIGURE 19

ESTIMATED FRACTURE STRENGTH VERSUS HYDROGEN CONTENT FOR VARIOUS TEMPERATURES

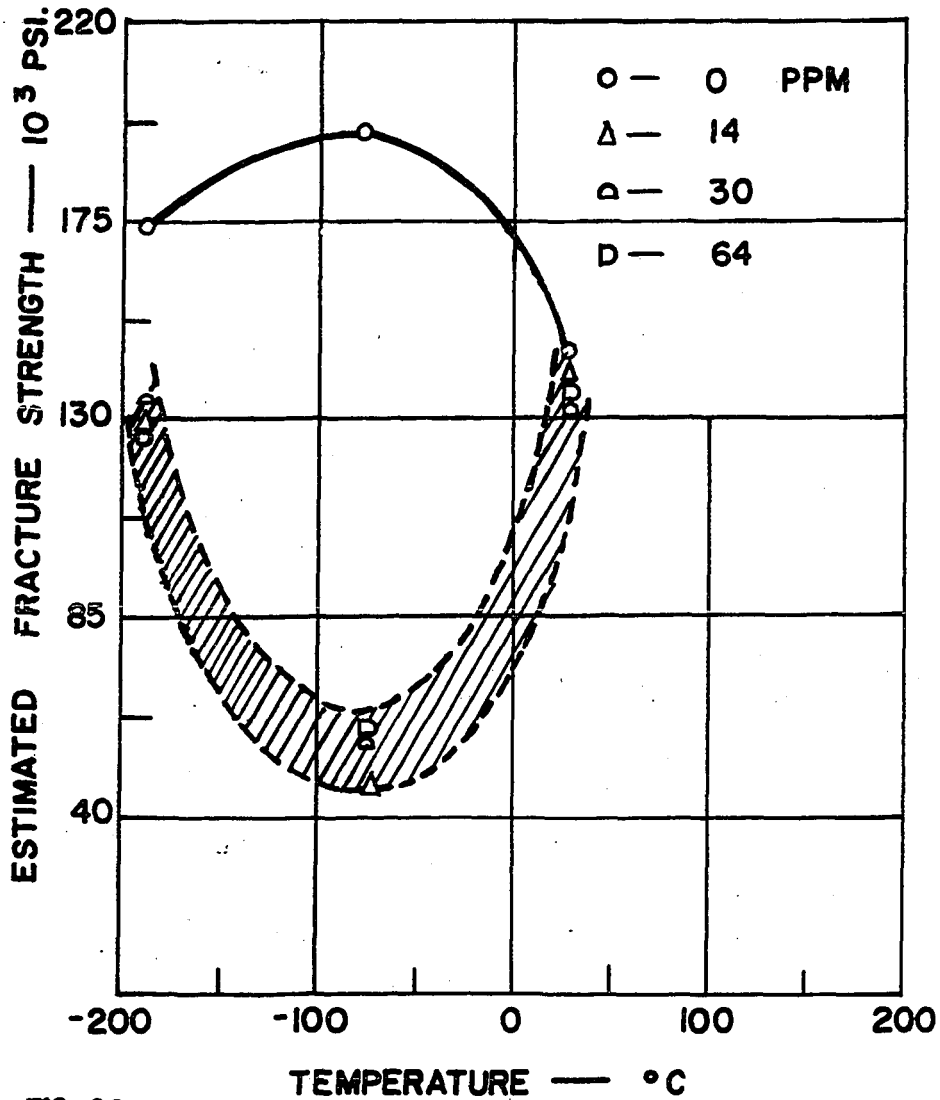


FIG. 20
FRACTURE STRESS VS. TEMPERATURE, RECRYSTALLIZED COLUMBIUM - HYDROGEN ALLOYS.

The second heat was used to investigate the mechanical property behavior of columbium as a function of hydrogen content and temperature. Thirty specimens were tested after various thermal treatments at a strain rate of 0.020 ipm/.815". As in the case of the third heat, it was found that the content of hydrogen required to effect a given degree of embrittlement increased in a roughly exponential way with increasing temperature of testing.

Some of the material was hydrogenated to 900 ppm; the resulting embrittlement was such that the material could not be machined. However a dehydrogenation anneal in vacuum of half a day at 650°C completely restored the original ductility. It was also observed that a sufficiently severe hydrogenation fragmented the columbium.

Since the second heat was hydrogenated to hydrogen contents in excess of 100 ppm, the ductility minimum was not observed in this material. However the fracture stress minimum exhibited in Figures 16 and 20 was observed in the data of the second heat. The relevant data from the first heat is consistent with these observations. No yield points were observed in testing the first and second heat material except an evident contamination yield point in the case of some of the first heat material. None of the first or second heat material was recrystallized.

The contamination yield point occurred as follows. Some finished specimens of the first heat were given 825°C

and 700°C anneals in high vacuum. Stringent cleanliness precautions were observed. The pressure at the (necessarily cool) ion guage was 2×10^{-5} mm Hg. The specimens annealed at 825°C exhibited a yield point about five times as high as that of the specimen annealed at 700°C. Annealing in even much poorer vacua produced no yield point below 500°C, although at 500°-600°C the stress-strain curve exhibited a sharp corner at the yield. Thus the yield point did not appear at temperatures where it should have already returned (13) if it were to appear. Annealing a rod of the first heat in a sealed iron pipe in air produced no yield point after recrystallization at 1150°C. Thus it is evident that the yield point was produced by outside contamination. A rod of the second heat from the same supplier annealed with the 700°C specimen likewise showed no yield point. Thus it is evident that by annealing finished specimens of columbium en vacuo above 600°C a spurious yield point may be produced, probably by the very potent hardener, oxygen.

What evidently happened is as follows. The residual gas contaminant strengthened the subsurface of the gage section by solid solution hardening and Cottrell locking, according to its interrupted diffusion contour. On loading the specimen, yielding occurred in the interior of the gage section, concentrating load on the subsurface region which then yielded so as to exhibit a yield point, perhaps through this mechanism as well as contamination.

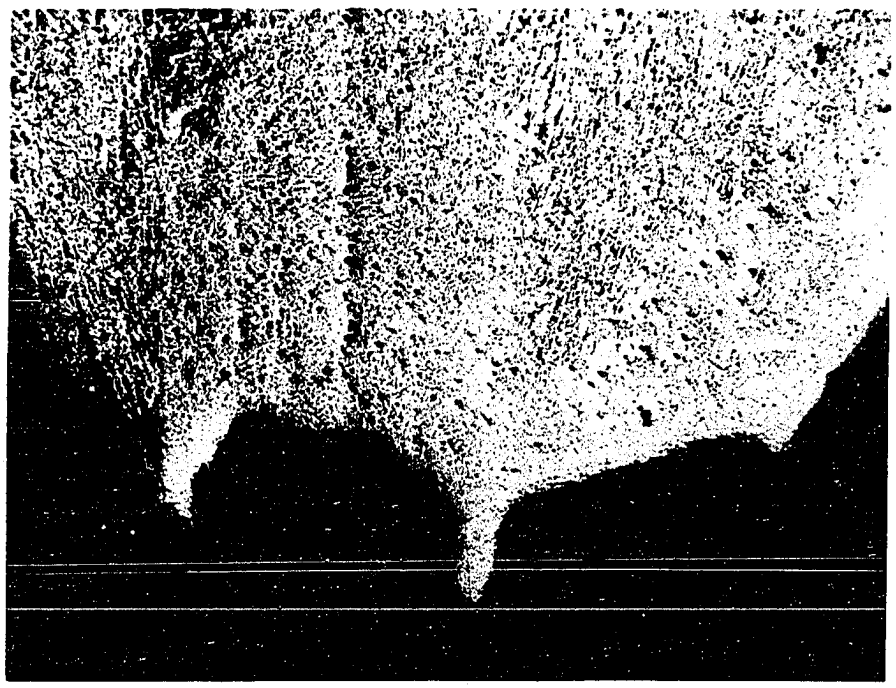
Results of Metallographic Investigation

Metallographic studies were pursued in parallel with the investigation of mechanical properties. Figures 21 and 22 are representative of the results. Figure 21 consists of two photomicrographs of the fracture region of a sample of pure columbium. One sees a few voids in the material and a region of slip in the enlargement. Figure 21 is presented for the purpose of comparison to Figure 22, so as to exhibit the effect of hydrogen.

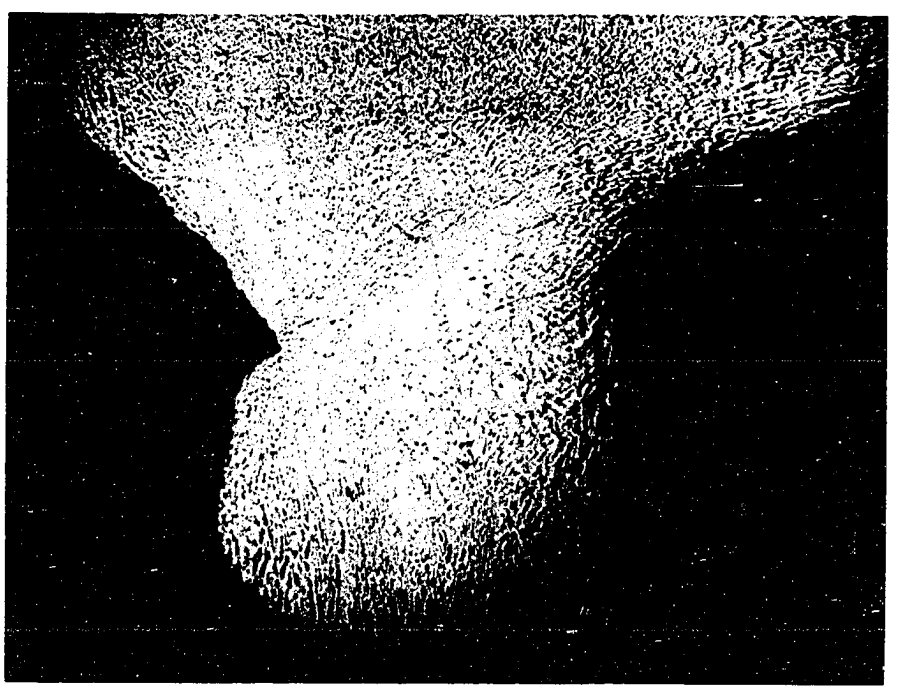
Figure 22 consists of two photomicrographs of columbium hydrogenated to 660 ppm. Note the high void density and flake-like cavities. One of the flaké-like cavities can be seen as the evident result of radial tensile stresses resulting from the blockage of slip. It is evident that hydrogen is effecting crack initiation, the cracks subsequently becoming extinguished. The second phase can be seen as a superposition of flakes on the elongated grain structure of the swaged material.

Results of Prestrain Investigation

Specimens of various conditions and hydrogen contents were prestrained various amounts at room temperature and then fractured in tensile tests in liquid air. This procedure produced no change in the observed fracture stress of the pure stress-relieved or recrystallized columbium. However, any plastic strain eliminated the ductility minimum observed in the third heat stress relieved material.



50 x.

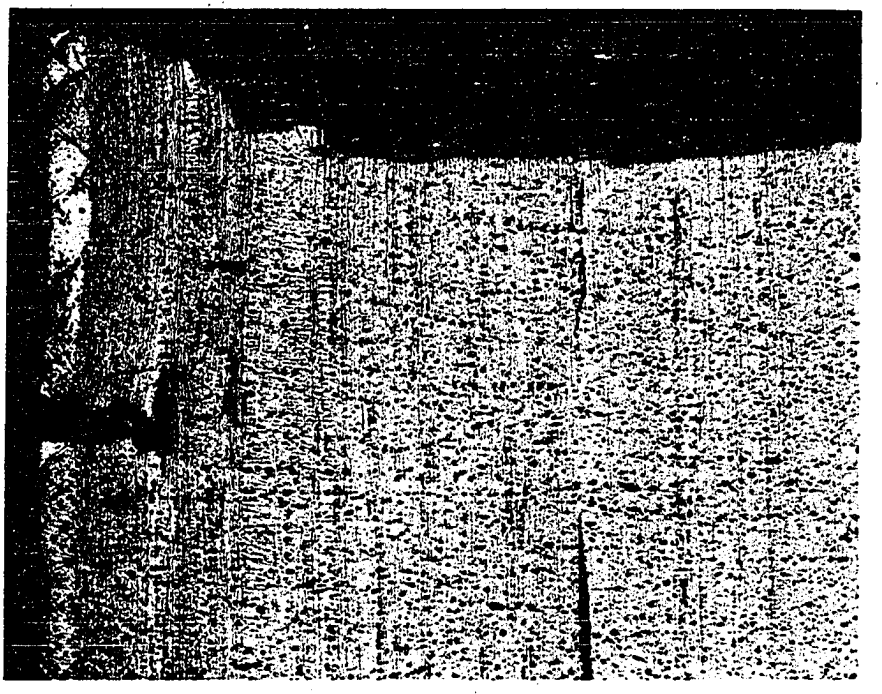


250 x.

CLOSE-UP OF TIP. SEE FIGURE 22.

PHOTOMICROGRAPHS OF PURE COLUMBIUM. FRACTURE REGION, SPECIMEN AXIS VERTICAL

FIGURE 21.



50 x.

250 x.

CLOSE-UP OF LEFT CENTER CRACK IN 50 x.
NOTE THE FLAKE CRACKS AND BLOCKED SLIP

MICROSTRUCTURE NEAR FRACTURE SURFACE OF PULLED SPECIMEN. STRESS WITH GRAIN.
660 PPM. HYDROGEN.

FIGURE 22.

The data derived from the prestrain investigation is given in Tables III and IV. Table III gives the prestrain data for third heat stress relieved material hydrogenated to 41½ ppm. Table IV gives the results of other prestrain tests on material of various hydrogen contents and condition.

TABLE III

PRESTRAIN RESULTS FOR THIRD HEAT STRESS RELIEVED MATERIAL HYDROGENATED TO 41½ ppm

Room Temperature Prestrain (Per cent Elongation)	Tensile Test Results at -190°C	
	Percent Reduction of Area	Fracture Stress lbs./sq. inch
zero (stressed elastically to 90% of yield)	53%	229,000 psi
0.075%	3%	139,600 psi
1.07%	1%	139,400 psi
3.15%	4%	145,200 psi
9.5%	4½%	148,000 psi

The results listed in Table III show that any plastic strain at all greatly reduced the fracture stress from its value of 225,000 psi at -190°C for the pure material that was not prestrained.

The prestrain results are significant to the theoretical interpretation contained in Chapter VI.

TABLE IV

PRESTRAIN RESULTS FOR THIRD HEAT MATERIAL OF VARIOUS CONDITION AND HYDROGEN CONTENT

Material Condition	Hydrogen Content, ppm	Prestrain, Percent Elongation	Reduction in Area Change	Fracture Stress Change
Stress Relieved	½ or less (pure material)	10.58	insignificant	insignificant
Stress Relieved	72	4.78	insignificant	insignificant
Stress Relieved	151½	3.33	insignificant	insignificant
Recrystallized	½ or less	13	insignificant	insignificant

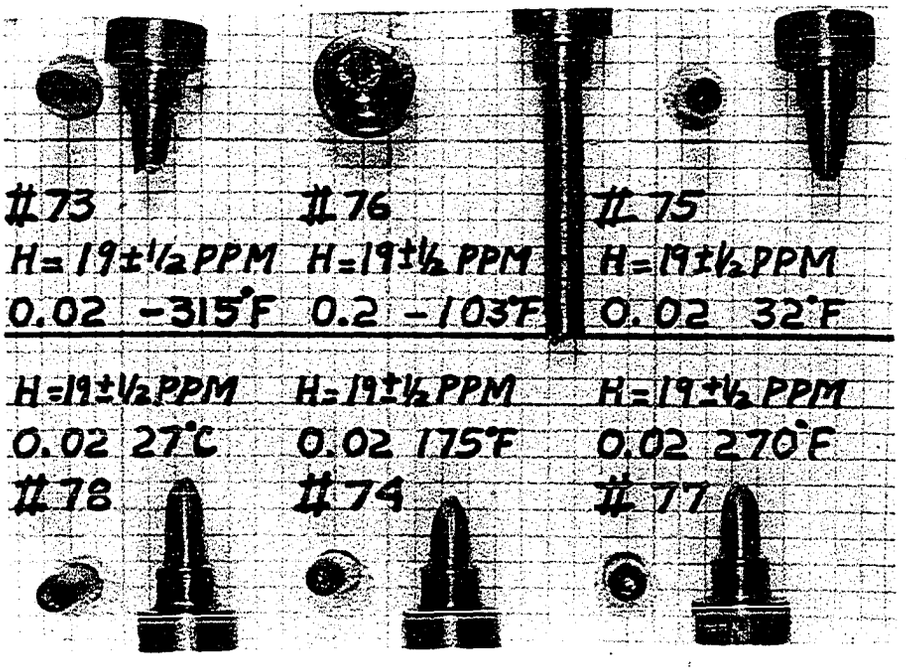
The pure columbium in both conditions was ductile, but the columbium with hydrogen contents of 72 and 151½ ppm was brittle, at -190°C, in conventional tensile testing. Reduction of area was 3-5% for the higher hydrogen contents.

The Multiple Cracking Phenomenon

A multiple cracking phenomenon was observed in both the stress relieved and recrystallized material of the third heat. The other material of the first two heats tested was not tested in the range of hydrogen content and temperature in which this phenomenon was observed. The phenomenon was as follows: Many cracks were seen in fractured tensile specimens besides the cracks that managed to traverse the gage section completely before all of the others. On metallographic examination very many more cracks are seen to have

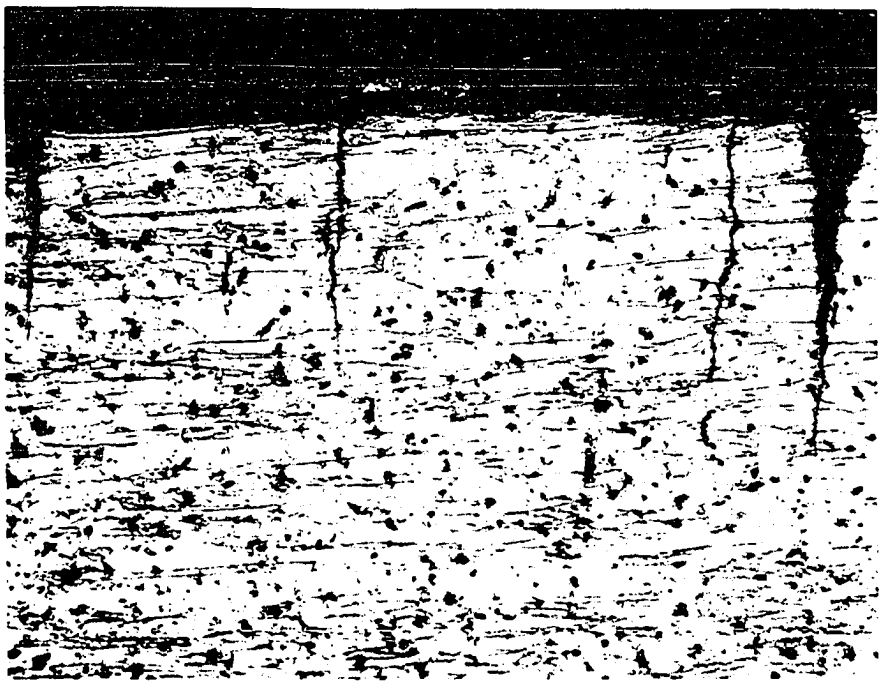
initiated and been extinguished while still of microscopic size. Figure 23 is a photograph of six mounted specimens, including the most severe case of multiple cracking. In the photograph the specimen number, hydrogen content, crosshead speed in inches per minute and testing temperature are printed beside the mounted specimen. Figure 24 is a representative photomicrograph of the gage section of a fractured specimen exhibiting the multiple cracking phenomenon. Uncompleted cracks extending part way across the gage section of the tensile specimen were sometimes observed in room temperature tests, but not in any degree of profusion such as in Figure 23.

The multiple cracking phenomenon is caused evidently by the variation in favorability toward crack propagation resulting from inhomogeneities on a microscopic scale to be found in a metal. In a sufficiently ductile metal a microcrack which begins to propagate due to locally favorable stresses will, after it exhausts the region of favorability, cease to propagate due to the growth of the plastic work term of the free energy of the microcrack. In a sufficiently brittle metal, on the other hand, a microcrack will continue to propagate once its propagation begins. The cessation of crack propagation in ductile metals and resulting phenomena are described in H. C. Roger's two studies of ductile failure (31, 39). Due to the presence of a positive feedback in the growth of the plastic work term in the free energy of the



BROKEN SPECIMENS, STRESS-RELIEVED MATERIAL.
HEAT 3.
(NOTE No. 76 WHICH IS OUR MOST PRONOUNCED EXAMPLE OF MULTIPLE CRACKING.)

FIGURE 23



PHOTOMICROGRAPH (250x) OF A SPECIMEN EXHIBITING THE MULTIPLE CRACKING PHENOMENON. NOTE THE MANY CRACKS ARRESTED ON A MICROSCOPIC LEVEL.

FIGURE 24

microcrack, a microcrack which propagates in one grain may cease to propagate in the next due to differences in lattice orientation and defect distribution. Thus in a region of hydrogen content, temperature and strain rate, many microcracks commence propagation only to cease propagation when the crack enters a region of unfavorability. A few of these cracks grow to visible dimensions.

The multiple cracking phenomenon occurred at the temperature for strain aging in the tensile test, during the transition with increasing hydrogen content from the ductility of the pure metal to the complete embrittlement occasioned by a sufficiently large hydrogen content. Mincher and Sheely (40) found that in columbium at conventional strain rates, the phenomenon of strain aging during the tensile test occurred as a maximum at a temperature where the diffusivity of the additive concerned was about 10^{-12} cm^2/sec. This level of diffusivity for hydrogen in columbium is attained at about -75°C, or approximately the temperature of the dry-ice-alcohol bath. At the temperature for strain aging in the tensile test the populations of the Cottrell atmospheres of the moving dislocations are at a maximum, and the surfaces of the growing microcracks receive hydrogen from the coalescence of dislocations at a maximum rate. This maximum of hydrogen supply to the growing microcracks is one of the evident reasons that the multiple cracking phenomenon and hydrogen embrittlement occur at the

lowest hydrogen contents at the intermediate temperature of -75°C. Another reason may be the prevention at low temperatures of the segregation of hydrogen from the volume of the metal to defects by the loss of atomic mobility of hydrogen with progressively decreasing temperature.

Silent Brittle Fracture

At high hydrogen contents at room temperature, where the ductility of pure columbium was very great, fractures of brittle form were observed to occur silently. Reduction of area was slight and necking did not occur. In the usual circumstances of brittle fracture the speed of crack propagation is considerably greater than the speed of sound in air. Thus there is a sharp report from the motion in the air of the edges of the fracture surface and the filling of the crack by the atmosphere. However this report was absent in the ambient temperature tensile tests of this investigation. The fracture, unlike normal brittle fracture, was often incomplete in that a small section of the specimen remained unbroken after a crack had nearly severed the gage section of the specimen. Occasional cracks were observed in addition to the crack that severed the specimen. These cracks extended part way into the gage section of the specimen.

The explanation is evidently that the columbium matrix remains ductile even in the presence of the second phase of the columbium-hydrogen system. The cessation of crack propagation that would occur in this ductile matrix is

counteracted by crack initiation at the second phase flakes and microcracks as discussed in Chapter VI. Thus the crack is conducted in a manner of ductile rather than brittle failure across the tensile specimen, similar to the manner of growth of the central crack in H. C. Rogers' study of ductile failure (31). The spontaneous fragmentations produced by very high hydrogen contents and observed in this investigation occurred in a manner similar to the fractures described above (see Figures 22-24).

Time-Temperature-Transformation Behavior

There is the possibility of hydrogen embrittlement by formation of Guinier-Preston zones on cooling. A test in which a specimen was step-cooled contra-indicated this. A tensile specimen containing 41½ ppm hydrogen was immersed in a dry-ice-alcohol bath while inserted in the low temperature tensile testing fixture described in Chapter III. After several minutes had elapsed the dry-ice-alcohol bath was poured out and liquid air immediately poured in. The tensile specimen was fractured in the liquid air and exhibited the same mechanical properties and ductility as material of this hydrogen content tested at liquid air temperature in the usual manner.

While the absence of an effect ascribable to precipitation in the above test is some indication that the embrittlement observed in this investigation is not due to a precipitation phenomenon in the usual sense, the test was

crude and calculations indicate that cooling rate was not adequately controlled. The adequate control of cooling rate in the case of specimens sufficiently large to give accurate results does not seem practicable. Thus this test does not give an adequate basis for a conclusion.

Yield Strength and Yield Point Phenomena

The pure recrystallized third heat material exhibited a yield point at room temperature and -77°C. This yield point was not affected by hydrogenation and disappeared as temperature decreased from -77°C to -190°C, as illustrated in Figure 25. Thus the yield point is not due to a hydrogen Cottrell atmosphere, and is due in a simple sense to a Cottrell atmosphere at all only if the Peierls-Nabarro resistance commences after the segregate forces are overcome; otherwise the two shear resistances would be more additive than substitutive. Then one could have the frictional resistance rise with temperature decrease faster than the restoring force of the displaced atmosphere, thus masking the latter at lower temperatures. The atmospheric restoration force would also vanish above the strain aging temperature for the (supposedly pure) atmosphere. Thus the yield point would be seen only over a finite temperature interval depending on history and analysis.

There is a possibility that the diminution of thermal agitation at low temperatures creates a large and necessarily variable freeing time for partially freed dislocation loops.

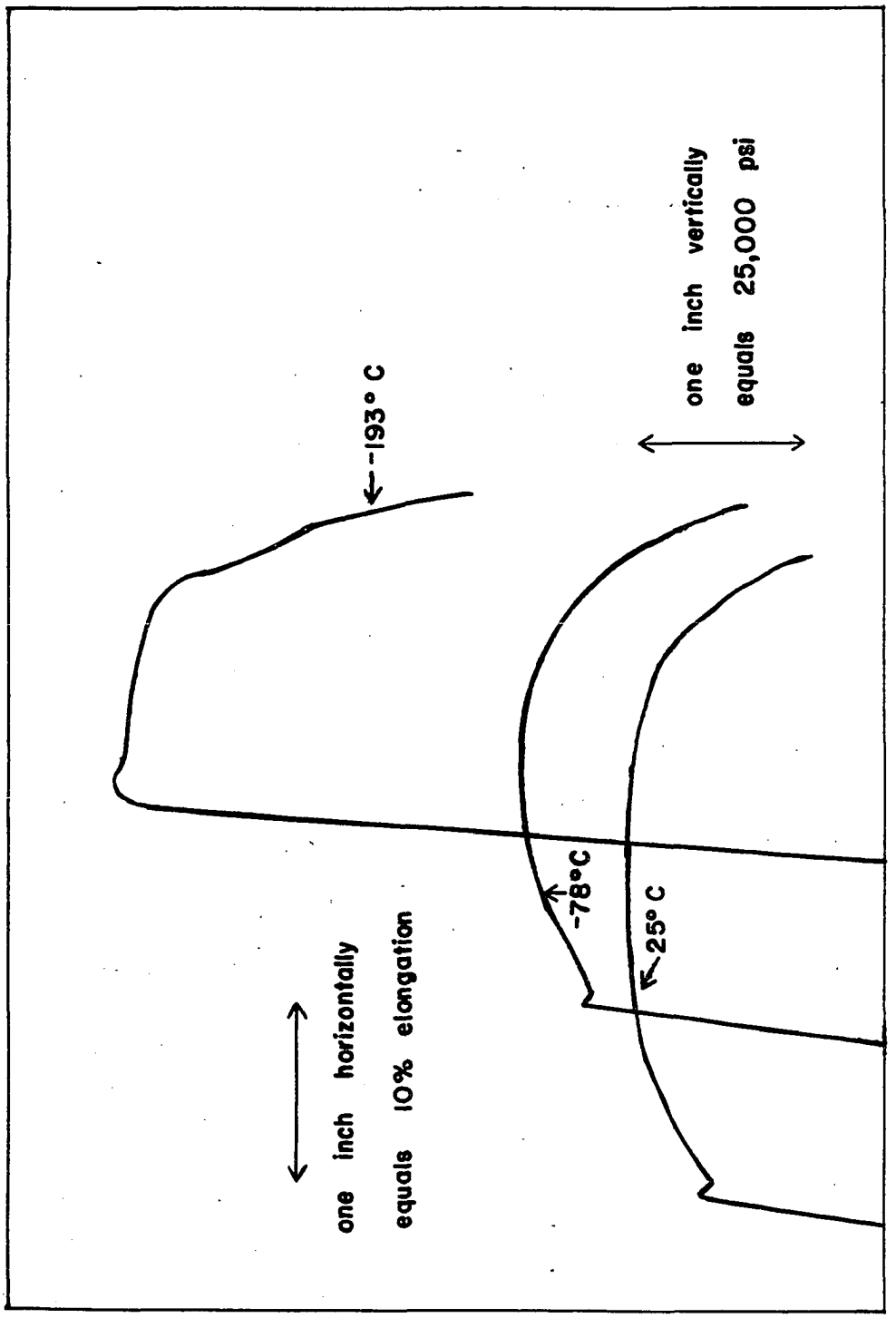


FIGURE 25. TENSILE STRESS-STRAIN CURVES FOR RECRYSTALLIZED COLUMBIUM, 0 PPM HYDROGEN, ASTM GRAIN SIZE 6-7.

Then, according to the randomness of thermal excitation, dislocation loops would break free over an interval of time. If this interval of time becomes, at low temperature, of the order of the time required to attain 1% strain during the tensile test, the variation of yielding time from point to point in the metal would become large enough to spread out or "smear" the yield point into the long, low bulge observed in the -190°C tensile tests. This possibility would apply also to the Wessel type yield point mentioned in the following paragraph (15).

There is also the possibility of a Wessel type yield point (15). This is a yield point produced by the pileup of dislocations at a barrier at a limited rate, with perhaps an activation delay in the following dislocation multiplication on the other side of the barrier. When the pileups become sufficiently large so that a stress concentration of sufficient magnitude is built up to create an active Frank-Read source across the obstacle, a sudden profuse dislocation flow requiring a reduced applied stress results. The stress then drops from the momentary upper yield stress to the resulting lower yield stress until strain hardening has accumulated sufficiently to appear. This mechanism pre-supposes a small amount of plastic flow before the upper yield stress is reached. That this does indeed occur, can be seen from the stress-strain curves.

The proliferation of somewhat unidentical obstacles with decreasing temperature and the diminution of freeing

thermal agitation would explain the disappearance of the yield point at low temperature. The variations in microscopic upper yield strength would by producing the yield point locally at different levels of applied stress smear the yield point into a long low bump such as is observed in the liquid air tests.

The critical shear couple to produce a Wessel yield point at a grain boundary for instance would depend on the orientations of boundary and adjacent slip planes, segregates that form at the couple, etc. The achievement of the couple will depend on the grain size and the proximity of adjacent pileups and slip bands together with the applied stress. If the minimum of the required applied stress as a function of these variables broadens out at low temperatures and develops serrations or if inhomogeneities develop to split up the minimum, then smearing is to be expected. There is also the possibility of a large, randomly varying yield activation time mentioned before. Residual stresses by varying from point to point in the metal on a microscopic scale will smear any yield point; thus the absence of a yield point in the stress relieved material.

Strain Aging

The strain aging behavior of columbium and columbium-hydrogen alloys was studied by the yield point return method. The strain aging behavior observed is best explained by a Wessel type yield point, although one might be able to fabricate an explanation from the cross-slip theory of the yield

point (41, 42). Begley (13) and Tankins and Madden (14) found an activation energy for the return of the yield point of 27 kcal/mole, whereas Wilcox (12) found an activation energy of 8-11 kcal/mole. The former value implies a Cottrell atmosphere of oxygen as the agent of strain aging and the latter value implies a Cottrell atmosphere of hydrogen.

In the present study three specimens, one with ½ ppm hydrogen or less and the others with 4½ and 8½ ppm hydrogen (all from the recrystallized third heat material), were pulled at room temperature. By measuring the time for yield point return as a function of aging temperature, an activation energy of 18 kcal/mole without hydrogen and 22 kcal/mole with hydrogen was determined for the process. The results of these tests are presented in Table V. The constant factor increased by a factor of about 10^3 on hydrogenation also.

TABLE V

EQUATIONS FOR THE YIELD POINT RETURN IN COLUMBIUM[a]

Hydrogen Content of Columbium, ppm	Equation for Yield Point Return
less than ½	$\frac{1}{t} = 8.7 \times 10^9 \times \exp(-18{,}000/RT)$
4½	$\frac{1}{t} = 9.3 \times 10^{12} \times \exp(-22{,}800/RT)$
8½	$\frac{1}{t} = 2.1 \times 10^{13} \times \exp(-22{,}600/RT)$

[a] T is the absolute Kelvin temperature.
t is the approximate time of yield point return, in hours, as determined from a number of criteria.
R is the ideal gas constant in cal/mole-deg. K.

Times of aging were all greater than 20 minutes and very rough correction was made from the thermal relaxation time observed for a thermometer. Thus thermal lag times are a lesser source of error than in previous works where times of 6 minutes were used without correction for thermal lag. However three specimens do not provide conclusive evidence. The yield point return was determined by the consensus of several criteria.

The effect of hydrogen in our data, and the discrepancy between these data and other works, can be explained on the basis of a Wessel yield point. On yielding the Frank-Read sources activate and slip bands form. If yielding is stopped stresses remain "frozen in" at the slip band and pileup ends so that if there is immediate reloading yielding recommences at the final stress level of the previous time. However if sufficient time is allowed to elapse the drift of dislocations, perhaps at an initially rapid rate, relieves the residual stresses. Thus the longer reloading is delayed, the more stress must be applied to return the residual stresses to their initial values on unloading.

The dislocation creep that relieves the residual stresses will be accelerated by heating. The dislocation will be slowed in this motion by Cottrell atmospheres. This interaction will in general be complex and dependent on history and analysis. The addition of hydrogen to such an atmosphere would be expected to change the kinetics of the motion, or what one might call the "activation group" of the dislocation,

which depends on analysis and history, not necessarily changing the heat of activation to that of hydrogen diffusion. One could thus obtain a different result for each history and analysis tested. Thus this set of mechanisms can explain the divergent data of columbium strain aging.

One should keep in mind of course that the Cottrell atmosphere and other strain aging mechanisms can change with straining temperature. A hydrogen contribution to the height of the yield point should appear below -75°C and annealing in a lower temperature range should restore the hydrogen contribution to the yield point after straining. Our aging took place in the 75°C range.

Strain Aging and The Effect of Hydrogen on Strength

Above the -75°C strain-aging temperature hydrogen does not strengthen columbium. The hydrogen atoms can adjust too rapidly to dislocation motion to maintain a retarding force. Below this temperature a maximum strengthening of about 20% is observed at approximately 40 ppm hydrogen. This maximum represents the optimum hydrogen atom spacing for dislocation pinning at the -190°C testing temperature. There is in general the possibility of an effect due to Guinier-Preston zones, however. At the strain aging temperature the maximum of strain rate dependence expected is observed, but the exact temperature of the maximum of the tensile and yield strengths was not found because of the widely spaced testing

temperatures employed. Also, the multiple cracking phenomenon complicates the mechanical property dependence at this temperature.

Additional Results

Low strain rate hydrogen embrittlement was not observed in columbium of the histories and analyses tested and for the range of strain rate employed of this investigation. Delayed failure was not observed in two specimens of columbium hydrogenated to 455 ppm hydrogen and held an hour at room temperature at a stress level near the fracture stress.

The fracture surfaces of specimens broken in -190°C tensile tests were of sparkling appearance, indicating transgranular fracture. Above -75°C, however, failure occurred by ductile processes and fracture surfaces were dull.

From data on sheet specimens of the first heat and as implied, but not proven, by the multiple cracking behavior of hydrogenated columbium, hydrogen does not greatly increase the notch sensitivity of columbium. Above the ductility transition columbium is not notch sensitive in the pure state; below the ductility transition notch sensitivity is expected.

Annealing a rod of dimensions 1 cm x 4 cm, sealed in an iron pipe, for an hour at 1150°C in air produced a ductile specimen. The annealing treatment was carried out in this manner because there was no vacuum furnace available which could be operated at this temperature. This specimen was

fully recrystallized but exhibited no yield point. Calculations from contamination hardening data (16) indicated that the gage section of the specimen was not contaminated by the treatment. There was very little oxidation of the columbium rod. This procedure is indicated as an expedient for the treatment of columbium (and no doubt some other metals) in the absence of vacuum equipment. The treatment was evidently equivalent to an anneal in impure nitrogen.

CHAPTER VI

THEORETICAL DISCUSSION

The Determinants of Ductility

There is a critical level of applied stress depending on type and treatment of a metal at which a microcrack will propagate. There is also a level of applies stress at which dislocations will begin to move and multiply so as to produce plastic flow. These two stress levels, and to a lesser extent the strain hardening exponent, determine the strain at which crack propagation occurs, and thus the ductility. When, during the course of the tensile test, the yield strength is attained, plastic flow commences. Thereafter, the applied stress must increase for straining to continue, by an amount dependent on the strain hardening exponent. If the ductility is great, maximum load will be passed without failure and necking will occur, the stress at the minimum cross section increasing the more rapidly. At length the stress level is attained at which a crack will traverse the specimen. The smaller the difference between yield and fracture strengths and the larger the strain hardening exponent the sooner or the lower the strain at which this will occur.

Starting from very elementary considerations one can obtain a mathematical statement of the above, assuming fracture occurs at or before the necking strain is attained on the engineering stress-strain record. One writes the equation of the true stress vs. true strain curve. If F is the theoretical fracture stress, K the stress concentration factor of the mechanism of crack initiation, e the fractional elongation at failure, S the nominal or engineering stress at failure, Y the yield strength or stress at the end of the lower yield point trough if such exists, n the average strain hardening exponent and L the strain at which the yield stress is taken, then:

$$F/K = S(1 + e) = Y \cdot \left((e - \tfrac{1}{2}e^2)/ L \right)^n$$

Thus an increase in Y or K or n will decrease e and thus the ductility. Necking introduces a complication, but one might devise a change of variable to extend the formula to large ductilities.

Thus an additive which does not at all affect the microcracks can embrittle a metal through strengthening; likewise an additive which does not impede dislocation transport can embrittle a metal by intensifying the concentration of stresses at the microcrack vertices and thus lowering experimental fracture stress. There are then these two aspects to embrittlement: Loss of ductility by strengthening without microcrack interaction and loss of ductility by microcrack interaction without strengthening. These aspects will of course generally both be present in a given problem.

The influence of hydrogen on columbium is one more of microcrack interaction than of strengthening. Hydrogen causes the engineering stress-strain curves to terminate "prematurely" without significantly affecting the yield strength. There is, however, a significant strengthening effected by hydrogen at about -75°C, due to strain-aging strengthening during the tensile test. Hydrogen has a greater effect on fracture stress than on yield strength in the case of columbium.

For the case of vanadium, which is immediately above columbium in the periodic table, the effect of hydrogen may be one more of strengthening than of microcrack aggravation. Eustice and Carlson (24) found a large strain-aging strengthening due to hydrogen at about -75°C. Although they do not consider the matter themselves, what data they present show a fracture strength minimum connected in the expected manner with the strain-aging strengthening. The minimum may be much less pronounced than in columbium.

A similar study in depth is lacking for tantalum, the lowest of this group of three vertically in the periodic table. With the limited variation of electronic structure down this group such a study might give insight as to the significance of atomic structure to ductility.

Experimental Difficulties in the Measurement of Fracture Stress

As straining progresses the microscopic inhomogeneity of a metal increases (31,39) with the result that the stress

concentration factor becomes large in microregions. Thus a crack can nucleate, exhaust the local stress concentration, but thereby grow sufficiently large (depending on the course of change of crack geometry) to continue propagation at the unmagnified applied stress. Thus the experimental fracture stress appears to be lower than the critical stress for the microcrack alone. Furthermore, in such as the silent fractures with rounded-terminus strip-chart records, Griffith fracture propagation is not macroscopically attained. In such cases one does not actually attain fracture stress in the sense above, and the failure stress one calculates is lower than the Griffith failure strength, on this ground alone. In cases not exhibiting a definite curvature peak or break-off indicating failure, an experimental fracture strength cannot be calculated.

The central crack that often appears in highly ductile specimens (31,39) furthermore gives a negative error in the determined fracture strength as its extent cannot be measured at the proper point on the stress-strain curve. It also introduces a macroscopic stress concentration factor, partially eliminated by plastic flow, in regard to the material at its edge. Also since the reduction in area is measured in a precision shadowgraph, the perimetric convolution introduces an additional negative error into the fracture strength.

All of these errors, due to the inhomogeneities of plastic deformation, are of the same sign and grow with

increasing ductility, until at 90% RA the fracture strength is a quantity of indeterminate value and significance. However, perhaps fortuitously, we observe pronounced minima of fracture strength at constant hydrogen concentration at the strain aging temperature. This means that the true fracture stress, defined as the stress to render microcracks in homogenuous material of critical size, exhibits even more pronounced minima over the temperature-hydrogen content plane than we have observed. Thus our conclusions are reinforced by consideration of the errors. The situation might have been largely otherwise for Eustice and Carlson (24).

The General Effect of Hydrogen

The effect of hydrogen is evidently to aid crack initiation and propagation in proportion to the extent of the hydrogen supply to the microcrack vertex. This is dependent on hydrogen concentration but for a given hydrogen concentration is also dependent on temperature, the effect being a maximum at about the strain-aging temperature where the Cottrell atmospheres are retained at maximum size by the dislocations coalescing into Stroh or Cottrell cracks.

The presence of an expanded second phase presents an obvious explanation for embrittlement at high concentrations of hydrogen. It may also explain a portion of the lower concentration embrittlement in view of the uncertainty in the solubility of hydrogen in columbium. There was no indication of this from the step-cooling test described earlier,

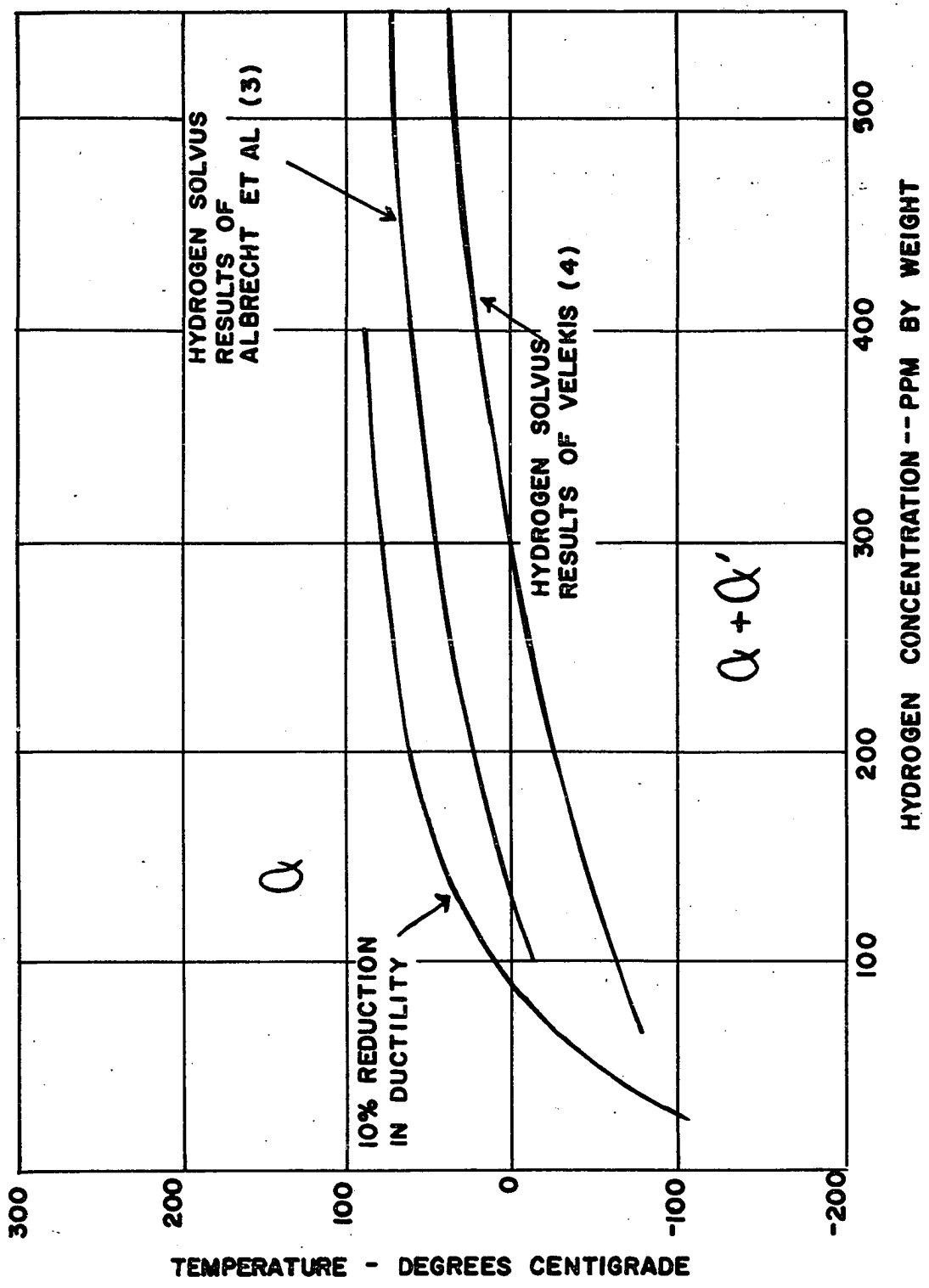


FIGURE 26. THE RELATION OF DUCTILITY TO HYDROGEN SOLUBILITY IN THE Cb-H SYSTEM. (10% REDUCTION IN DUCTILITY CURVE MAKES THE HYDROGEN CONTENT, AT A GIVEN TEMPERATURE AT WHICH THE PERCENT REDUCTION IN AREA HAS DECREASED BY A 10% FRACTION FROM ITS VALUE FOR THE PURE COLUMBIUM)

but since cooling rates were not closely controlled, the negative result was not necessarily conclusive. Thus a brief account of the second phase and its effects follows.

The Second Phase

The high-concentration embrittlement of columbium by hydrogen is readily explained by the presence of a second phase (see Fig. 26). A phase diagram of the columbium-hydrogen system exhibits a bell-shaped region of two phases, a single phase occurring elsewhere. This second phase precipitates as flakes on (100) type planes (43) and is expanded about 10% by volume compared to the saturated matrix (3). The columbium atoms are practically immobile and as hydrogen clusters into the nucleus and the flake grows the resulting expansion must be relieved by plastic flow or crack propagation. Thus the second phase constitutes prestressed Griffith cracks on cleavage planes. It is then to be expected, as is observed, that failure will commence at a far lower stress at high hydrogen concentrations than at low hydrogen concentrations.

A large flake may render a microcrack near its rim of critical size, or a small flake may, through the higher energy and thus lower strength of its interface, initiate a crack at its rim which then overcomes the adhesion across the interface. The second phase is also an explanation of the peculiar manner of cracking exhibited by columbium. The maintenance of crack propagation in a ductile matrix in the

face of the plastic work term would depend on, among other things, the distribution of second phase flakes in front of the crack. In a transition region of stress and hydrogen content cracks would grow macroscopically large only to sometimes "pull out" on entering a region of few flakes. In a ductile metal a crack initiated in a region of high stress concentration will lose the ability to propagate (31,39) and will round into a spheroidal cavity if the stress and nature of the metal outside the region of initiation provide a sufficiently profuse dislocation flow to the vertex. Rogers (31,39) has studied the phenomena of ductile failure and presented an experimental paper thereon.

Figures 21 and 22, the photomicrographs of pure and hydrogenated columbium, respectively, described in Chapter V, exhibit the behavior indicated above. Several "pulled-out" cracks are shown. Note the consequences of the blocked slip in Fig. 22 and the flake-like cracks and the high void density. These features of Fig. 22 in contrast to Fig. 21 demonstrate the hydrogen-induced initiation of cracking, the cracks being subsequently extinguished by plastic flow.

The second phase might still explain the ductility minimum. There were differences in cooling rate between the liquid air and dry ice tests. The second phase could have been absent in the liquid air tests, while because of the slower cooling rate precipitation may have occurred in the dry ice tests. As mentioned earlier, however, results

obtained after step-cooling to -190°C tend to negate this hypothesis.

In the formulation of an explanation of the data on the basis of a precipitation of the second phase, one must consider also the results of the prestrain investigation. As noted before in Chapter V, any plastic strain eliminated the ductility restoration at liquid air temperatures. This can be explained as the provision by the prestrain of opportunity for hydrogen segregation into microcracks. The micocracks would be formed during straining, and any previous microcracks presumably would have been decomposed by the 500°C anneals coincident to hydrogenation. On the other hand, there has been a suggestion that the second phase is partly martensitic in nature (44). Thus strain induced precipitation is also possible.

It is to be noted that the prestrain data was taken with material having a hydrogen content of one-sixth the lowest estimate of the hydrogen solubility at room temperature in columbium (3). The second phase was not observed metallographically below 500 ppm, and the limited control of cooling rate during the low temperature tests was not mirrored in any irreproduceability of liquid air mechanical property behavior. Thus, while an explanation of the data on the basis of microscopic and submicroscopic precipitation cannot be ruled out, a submicroscopic interaction between hydrogen and microcracks such as is described later may be preferred.

Figure 26 presents for comparison the onset of appreciable embrittlement and two estimates of the solvus of the columbium-hydrogen system.

The Nature of Crack Initiation

When a stress is applied to a metal the basic set of lattice vectors is distorted and the lattice as a result is displaced from its lowest energy configuration. The energy levels available to its component particles are lifted, the particle energies are raised, and the necessary flow of energy quanta is provided by the straining mechanism. If a microcrack is created, for example by dislocation coalescence, the stress will be relieved adjacent to the free surface away from the edges, but will be concentrated next to the edges. Work against the interatomic forces is required to create the microcrack by separating the opposing surfaces. The relief of strain occurs roughly in the circumscribed sphere of the microcrack and the created surfaces occupy a disc, more or less.

When the microcrack enlarges, the region of strain relief grows and energy is liberated, but work is done against the interatomic forces at the crack vertex. This work is equal to the energy content of the new surface, plus any plastic flow work due to dislocation motion. However, since the amount of energy turned eventually into heat by the growth of the region of lessened strain varies as the cube of the crack diameter, but the work of surface formation provided by

the straining sources varies as the square, taking the microcrack as roughly circular, there will be a crack radius at which the straining source is sufficiently aided by the release of strain energy to result in crack initiation and, if the straining source is permitted to remain effective, propagation. This radius is termed the critical radius and one has the Griffith fracture theory.

Thus one can, by maintaining sufficient stress, cause the propagation of any microcrack. However, this energy criterion is not the sufficient condition for fracture, though it is a necessary one. There must not only be a mechanism which will cause the reclassification of energy as heat but there must be another mechanism by which this process will occur in a reasonable time. A mixture of hydrogen and oxygen will exist for a long time at room temperature without a spark.

The mechanism for crack propagation is the concentration of stress at the microcrack rim. Sufficient force must be at hand to break the interatomic bonds at the crack vertex. The effectiveness of a microcrack as an initiator of fracture can be expressed by the value of its stress concentration factor. At a stress of F/K, where F is theoretical fracture stress and K is the stress concentration factor of the microcrack, the applied stress will result in the initiation of fracture. Fracture is the successive breaking of interatomic bonds situated along a line advancing through the metal.

Thus the critical size of a microcrack depends on the sharpness of the crack vertex as well as applied stress. An energy-liberating mechanism can occur only to the extent permitted by its mechanism of occurrence. Further geometrical factors are injected by the manner in which absorbates and pseudonuclei wedge themselves into the microcrack vertex, which will be discussed in the next section. The Griffith criterion one obtains from the point of view of stress concentration is not experimentally differentiable from that obtained from free energy considerations, due to the inaccuracy with which one must proceed in the necessary task of counting each quantum once and none twice.

Once initiated, a crack may be extinguished. If dislocations are sufficiently generable and mobile their motion as the crack vertex approaches a Frank-Read source will act to round off the vertex and reduce the stress concentration factor; or, the plastic work term in the crack surface energy becomes large, depending on one's choice of criterion. If these dislocation bursts become sufficiently profuse crack propagation will cease, especially if the crack commenced propagation in a region of high stress concentration favorable to crack initiation. In cases where microscopic inhomogeneities produce high and variable residual stresses on a microscopic scale, one can then have phenomena such as "hairline cracking" or our competing cracks. The ductility transition temperature found in body centered cubic metals is

essentially that point in the decrease of temperature at which the yield strength rises rapidly but the fracture stress does not, and the above mechanism of crack propagation quenching ceases to operate.

Action of Hydrogen At The Crack Vertex

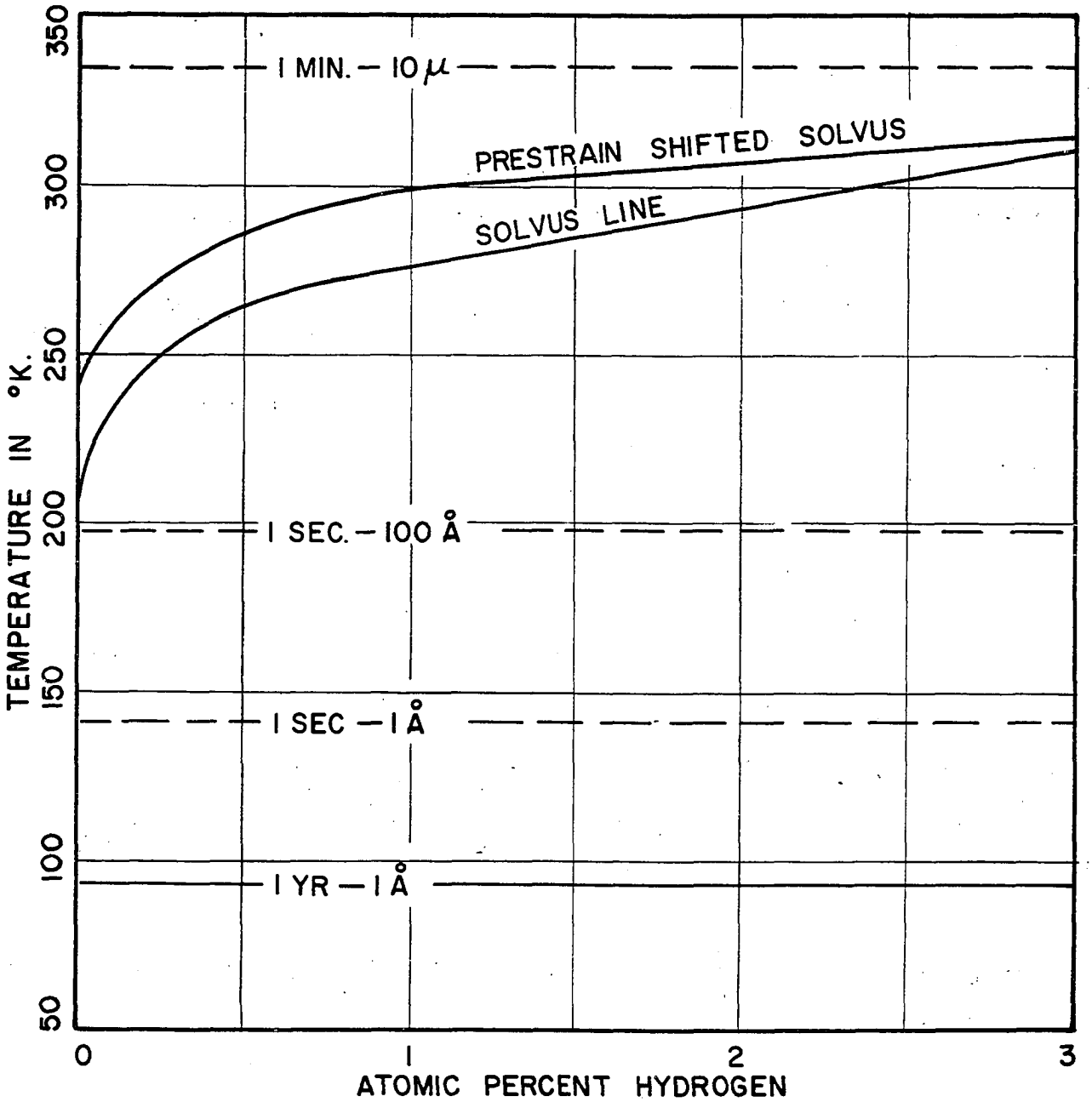
Hydrogen may segregate into microcracks by volume and surface diffusion, the latter from the point of Cottrell atmosphere delivery at the base of the microcrack or multiple dislocation. Depending on the relative magnitudes of chemical attraction and electronic repulsion forces hydrogen atoms may energetically prefer the region of tensile strain at the crack vertex, so as to form a Cottrell atmosphere in the region of tensile strain at a dislocation. This is to be expected as hydrogen is an interstitial which dilates the lattice. Hydrogen sites on the atomically clean surface of a recently formed microcrack may be expected to be much lower in energy than sites in the lattice in view of the strong chemisorption exhibited by gas-metal systems in general, regardless of the free energy of solution.

Hydrogen sorption on a microcrack surface, which will be atomically clean except for surface redistribution of Cottrell atmospheres and segregation from the metal lattice if the crack is old enough, will lower the surface energy. Since the surface energy is the work done in the breaking of an interatomic bond times the surface density of bonds, hydrogen effects a force tending to break the bonds at the crack

vertex. Thus from the stress concentration as well as energetic viewpoint hydrogen lowers critical or fracture stress for the metal. The work per atomic area of surface formation for the crack is the integral of the restoring force exerted by the "chemical bond" over the distance from zero stress to the point where the attractive force exerted by the bond has practically vanished. This distance is a few lattice spacings at most. The restoration force is initially small (Hook's law), increases to a maximum and then asymptotically vanishes. The maximum restoration force is the theoretical fracture strength times the atomic area on the plane. It is this maximum force which hydrogen must reduce by a general flattening of the curve of restoring force vs. distance, unless its effect on the integral is to be strangely localized. Thus there is at least a virtual maximum restoring force reduction by surface adsorbates in the microcrack. The force reduction is evidently a counterforce arising geometrically from forces of repulsion between the adsorbate atoms. Stress lines will originate at the hydrogen atoms drawn by the maximum adsorption forces at the crack vertex and add themselves to the dense array of stress lines just outside the vertex of the microcrack. If one has a notched beam in tension and one applies a mechanism exerting forces to expand or "break open" the notch, one will need a smaller tensile load on the beam to effect failure; thus the addition of stress lines to the concentration thereof at the vertex will reduce experimental

fracture strength and effectively increase the stress concentration factor.

Also, a simple calculation shows that the solubility of hydrogen with respect to pseudonucleus of the second phase at the microcrack vertex is halved or so from the macroscopic solvus at room temperature and reduced morefold below. Suppose one had a mechanism that applied stress on a microscopic scale so as to achieve hydrostatic tensions much in excess of the elastic limit. A hydrostatic tensile strain of 3½% would place the Cb atoms on the lattice of the expanded second phase. Then admission of the hydrogen to the lattice would permit second phase formation without the hydrogen doing the work of hydrostatic tension against the attractive forces of the columbium in the precipitation process. Thus the free energy of formation of the second phase would be changed so as to permit precipitation at lower concentrations. The extent of this change in solubility is given by exp. $(-\underline{E}/RT)$, where $\underline{E}$ is the energy or work of hydrostatic tension. If the work density of uniaxial tension is $\frac{1}{2}Ee^2$, where E is the elastic modulus and e is the strain, then although one is exceeding the elastic limit in terms of Hook's law the energy density of hydrostatic tension is approximately $3/2\ Ee^2$. At room temperature this quantity is about 440 cal/mole Cb. The strain energy must vanish at the critical temperature of the miscibility gap since the lattice constant differential must vanish there. Thus to a



POSSIBLE COURSE OF THE COLUMBIUM-HYDROGEN SOLVUS LINE, MAXIMUM PRESTRAIN SHIFT, AND TEMPERATURE LIMITS

Figure 27

crude approximation the free energy saving is proportional to $(T_c - T)^2$, and is given by:

$$F_f = 3\ E\ e^2\ (Tc - T)^2\ /\ 2\ (Tc - Tr)^2$$

where F_f is the change in the free energy per unit volume of formation of the second phase, e is the strain of precipitation at room temperature, Tc the critical temperature of the miscibility gap, T the temperature of interest, and Tr is room temperature.

The concentration shift of the solvus in the Cb-H system is given by:

$$\frac{C'}{C} = \exp\ (-F_f'/RT) \quad \text{approximately}$$

where C' is the new solubility after prestraining and C is the solubility under normal circumstances. The prime on F_f' signifies the free energy per mole of hydrogen rather than columbium, and is increased by the reciprocal of the atomic ratio, or atoms of H per atom of Cb. However this factor is ignored in Fig. 27 as one is not able to obtain the actual effect of the tensile strains (largely uniaxial) at the vertex of the microcrack and one might be somewhat conservative in one's estimate, in this case by 25-50% in the free energy.

Figure 27 shows the macroscopic solvus of Albrecht (3) and the nominal submicroscopic solvus discussed before. Also the horizontal lines give the temperature from the formula:

$$T = E/R \ln (Do \cdot t/a^2)$$

which comes readily from the Ahrennius diffusivity law. The time and characteristic distance printed on the line are substituted into the formula to give the approximate cutoff temperature for segregation processes of that scale. These lines serve as a guide together with the solvi, to relating the data to the mechanisms suggested for the embrittlement.

Thus Fig. 27 shows Albrecht's solvus (3) and a representative shifted solvus. The actual solvus is a matter of the Schrödinger equation applied to an assymetric many body problem and is not practically accessible, and the geometry of the crack vertex must remain poorly known. However, it is evident that a pseudonucleus of the second phase, which is expanded sufficiently to initiate considerably many lines of stress, may occur at the microcrack vertex, shifting as well as adding to the lines of applies stress concentrated at the crack vertex.

The effect of hydrogen segregation into a pseudonucleus on the value of K for the microcrack will depend on how the hydrogen distributes itself about the vertex and the accompanying expansive strains created. The segregation of hydrogen will evidently be accompanied by an expansion of the strained region of a kind which will not only displace the lines of stress from the segregate region but add lines of stress originating in the segregate to the concentration adjacent to the vertex and segregate. This, as in the case of the surface adsorbates, will decrease experimental fracture strength, although a rigorous proof requires a

microscopic elastic theory and knowledge of the atomic geometry at the vertex, as well as a semiclassical approach of known validity. One has atoms and not a homogenuous medium.

Thus by both surface adsorption and probably segregation hydrogen evidently lowers fracture strength by intensifying the concentration of stress lines next to the crack vertex. Thus fracture is initiated at a lower applied stress. However the propagation of the crack must be maintained. In the case of the surface adsorbate the crack will be slightly larger when the adatoms are left behind, and possibly sharper; surface diffusion of columbium atoms should not blunt a Stroh or Cottrell crack below 100°C in a reasonable time. However with the loss of counter-restorative force from the adatoms the atomic bonds may hold. Thus the adatoms must attain the new vertex by surface diffusion, permitting slow but accelerating crack growth until enough stress lines are crowded against the enlarged crack vertex to produce propagation without the aid of surface diffusion.

One also has the possibility of a divided microcrack, fracture being initiated on the other side of a segregate. Then lines of stress from the newly fractured region are shifted to the segregate, being then concentrated at the two sharp vertices extending into the segregate. This situation may result in immediate fracture of the segregate and creation of a considerably larger microcrack which will immediately propagate under the applied stress, especially after a

time delay for surface diffusion of adsorbates. Since the site energy on a surface will lower if additional attractive atoms are brought near, the site energy on the microcrack surface drops as the vertex is approached, rising subsequently at the vertex if repulsive forces dominate at closer approach. Thus a transfer of adatoms to the new vertex is to be expected, especially over the outer adlayers where binding is weak and diffusivity will be high.

Thus one may have crack propagation (although the crack may subsequently be extinguished as it passes a Frank-Read source) due to hydrogen adsorption and segregation by diffusion on the microcrack surface to the vertex, and to segregation of hydrogen to a pseudonucleus of the expanded second phase adjacent to the crack vertex. However, a rigorous proof has by no means been presented. The semi-classical treatment that is possible will be very complicated, and a rigorous solution is still prevented by the nature of the quantum-mechanical many-body problem.

Correlation of the Data With Observed Behavior

As temperature decreases with hydrogen content constant, the surface and volume microsegregates would eventually form, and evidently to the left of the macroscopic solvus of Albrecht (3). Thus one would expect the fracture strength to diminish with decreasing temperature as observed. By -175°C however the mobility of hydrogen in the Cb lattice would no longer permit this to occur by volume diffusion.

Thus one would expect the fracture strength to rise again as observed. The Cottrell atmospheres would cease to keep up with the dislocations below -75°C (40), except that the residual Cottrell atmosphere consisting of the balance between those hydrogen atoms trapped in the moving line void and those excited out by thermal agitation will still be dumped at the base of the microcrack by the coalescing dislocation. Thus as temperature decreases, one would have a maximum hydrogen supply to the microcracks at an intermediate point. The population of the Cottrell atmosphere increases as temperature decreases above -75°C, the "strain aging" temperature, as hydrogen atoms will segregate more and more to the less tightly bound outer sites about the dislocation. The population should be essentially pure hydrogen since, due to lower diffusivity, the other interstitial atoms should be left behind at 325°C. However at -75°C the same situation should occur with hydrogen and the population drop to the above noted minimum. With the maximum hydrogen supply occurring at perhaps -75°C it is comforting to observe a pronounced fracture strength minimum there.

With Stroh and Cottrell cracks forming at yield one expects the fracture strength to depend on the yield strength and the minimum in fracture stress observed may be the result of the ductility transition. The strain rate dependence of the fracture strength at -75°C for the recrystallized material, although in the desired direction, may likewise be the

result of the large strain-aging strain rate dependence of the yield strength at this temperature.

During the hydrogenation runs all material was annealed in the range 450-550°C. One would expect that Stroh and Cottrell cracks would be dissociated by this treatment and not reformed until the beginning of the tensile test. Thus the pre-strain results, as mentioned before, (any plastic deformation eliminated the ductility minimum) can be explained by the segregation of hydrogen prior to or during the cooling to liquid air temperatures, this being greatly reduced if the cracks are not formed until after liquid air temperatures are attained.

Due to the larger grain size at 45° to the specimen axis of the recrystallized material, the fracture strength of this material was expectedly lower. The Stroh or Cottrell cracks, the latter not without difficulty of interpretation, would be larger. Thus the concentration of stress lines at the vertex (of unchanged geometry) would be more dense. The equivalent hollow ellipse for the microcrack would be of greater eccentricity. With more dislocations in the microcrack, the Cottrell atmosphere population per unit length of the microcrack vertex would be greater. Providing surface adsorption is sufficient to provide an outer layer for rapid diffusion at liquid air temperatures, a greater vertex segregate would form for a larger Stroh crack, and thus the reduction in fracture strength would be proportionately greater.

The loss of the ductility restoration for the recrystallized material may be due to the effect of the larger vertex segregate in maintaining fracture strength reduction in spite of the low supply per dislocation of hydrogen at liquid air temperatures.

The mode of fracture at higher (room) temperatures indicates that some regions of the Cb lattice are prepared for brittle fracture and other regions, or rather the remainder of the lattice, are such as to extinguish cracks. One has an internal notching by the second phase and the proposed submicroscopic mechanism as well. Notch sensitivity is the result of the inoperativity of the extinguishment mechanism in the limit of experimental fracture strength approaching yield strength; then a tool mark or nearly microscopic scratch can initiate a crack that will manage to traverse the specimen. On the other hand if local microscopic conditions are maintained so that crack initiation can occur at much lower stresses, the subsequently extinguished cracks will produce only the voids of Rogers (31,39). Thus notch sensitivity has not been observed and is not to be expected much above the pure-Cb transition temperature in hydrogenated columbium.

Whereas our fracture strength data is adequately explained by the above theories, at the present stage of metallurgical theory it is not possible to decide whether this set of mechanisms is the proper set. Rather in view of the many defect types and the complexity of possible

interactions there may be several theories which will have to be assigned equal a priori validity.

Because of the lower diffusivity of other interstitials, having greater atomic radii and stronger chemical bindings, behavior such as has been ascribed to hydrogen will be seen only at superambient temperatures; furthermore, stronger dislocation interactions and lower solubilities will change the embrittlement picture presented.

CHAPTER VII

SUMMARY AND CONCLUSIONS

The mechanical properties of columbium and columbium-hydrogen alloys were investigated as functions of hydrogen content, strain rate and temperature. The primary results of this investigation are summarized following.

1. Hydrogen embrittles columbium. The amount of hydrogen required to effect a given degree of embrittlement increases exponentially, approximately, with increasing temperature. At 120°C hydrogen contents in excess of 400 ppm by weight are required to effect a significant decrease in ductility from that of the pure columbium. At ambient temperature, however, 80 ppm hydrogen will effect the same decrease in ductility. At -75°C, only a few ppm of hydrogen are required to effect this decrease.

2. Depending on analysis and history, there may be a ductility minimum, or rather a ductility restoration below -75°C. A few ppm of hydrogen, in the absence of a ductility restoration, will cause severe embrittlement of columbium at low temperatures. Thus the hydrogen contents common to commercial columbium may cause serious difficulties at low temperatures, depending on history and analysis.

3. Warming hydrogenated columbium sufficiently will result in decomposition of the embrittlement mechanism and restoration of the ductility as long as the elevated temperature is maintained. Vacuum dehydrogenation of columbium completely embrittled by hydrogen will restore the original ductility almost completely. There will, however, be a purity dependent permanent damage threshold. It was observed that the repeated hydrogenation of columbium will break up the metal, the faster the lower the purity. Also large hydrogen gradients, at least involving second phase formation, will break up columbium.

4. Low strain rate hydrogen embrittlement did not appear in the regions of strain rate, history and anslysis investigated. Delayed failure did not appear in the course of a limited investigation for this phenomenon.

5. Hydrogen has only a minor effect on the strength of columbium. A strain-aging-in-the-tensile-test effect on the mechanical properties exists due to hydrogen at the expected temperature of -75°C. Hydrogen has negligible effect on the strength of columbium above this temperature. Below this temperature hydrogen effects a mild strengthening of columbium. This strengthening exhibits a maximum of 10-20% near 50 ppm hydrogen. The yield and tensile strengths of pure and hydrogenated columbium increase slowly with increasing strain rate.

6. A yield point was observed in part of the columbium used in this investigation. The yield point changed into

a long, low bulge when the temperature was decreased from -75°C to -190°C. Three possible explanations are noted.

7. Strain aging in columbium and columbium-hydrogen alloys was investigated by the return of the yield point method. The activation energy for the return of the yield point on aging determined in this investigation was different from and intermediate to the values obtained by other investigators. A model for the yield point and strain aging by means of which these data can be rationalized is presented.

8. It was found in tensile testing that any degree of plastic prestrain at room temperature eliminated the ductility restoration at -190°C in columbium containing 41½ ppm hydrogen. Two possible explanations were suggested, one involving the segregation of hydrogen to microcracks formed in advance of tensile testing, and the other involving strain induced precipitation of the second phase of the columbium-hydrogen system.

9. A model is presented by means of which the data obtained in this investigation can be rationalized. The second phase of the columbium-hydrogen system is observed to effect considerable embrittlement within the two phase region of the columbium-hydrogen phase diagram. A volume expansion of ten percent is associated with the formation of the second phase. However, embrittlement is observed at hydrogen concentrations below the available estimates of the solubility of hydrogen in columbium. Thus a submicroscopic mechanism of embrittlement is suggested. Hydrogen

would segregate to microcracks, especially to their vertices. At the vertex the hydrogen atoms, by forces derived from the forces of attraction between the hydrogen atoms and the columbium atoms, would add stress to the stress concentrated before the microcrack vertex. This internal stress would then cause the microcrack to begin to propagate at a reduced external, applied stress.

REFERENCES

1. Smith, D. P. "Hydrogen in Metals," University of Chicago Press, Chicago, 1948.

2. "Technology of Columbium," (Symposium) edited by B. W. Gonser and E. M. Sherwood, John Wiley & Sons, New York, 1958.

3. W. M. Albrecht, W. D. Goode, and M. W. Mallett, "Reactions in the Niobium-Hydrogen System," Journal of the Electrochemical Society 106, (981-6), 1959.

4. E. Veleckis, Ph.D. Thesis, "The Thermodynamic Properties of the Systems Nb-H, V-H and Ta-H," Illinois Institute of Technology, January 1960, ASTIA No. AD 259037.

5. B. R. Queneau and G. A. Ratz, "Embrittlement of Metals," American Society for Metals, Cleveland, 1956.

6. F. Garofalo, Y. T. Chou & V. Ambegaokar, "Effect of Hydrogen on the Stability of Microcracks in Iron and Steel," ACTA MET 8, (504-12), 1960.

7. N. J. Petch, "The Fracture of Metals," Progress in Metal Physics, vol 5, (1-46), 1954.

8. A. H. Cottrell, "Theory of the Brittle Fracture of Steel and Similar Metals," Trans. Met. Soc. AIME 212, (192-202), 1958.

9. A. N. Stroh, "A Theory of Fracture of Metals," Advances in Physics 6, (418-465), 1957.

10. C. W. Balke, "The Corrosion Handbook," Wiley & Sons, New York, 1948, p. 621.

11. B. A. Wilcox, A. W. Brisbane, and R. F. Klinger, "The Effects of Strain Rate and Hydrogen Content on the Low Temperature Deformation Behavior of Columbium," Trans. ASM 55, (179-92), 1962.

12. B. A. Wilcox and R. A. Huggins, "Strain Aging Effects in Columbium due to Hydrogen," 1960 Columbium Metallurgy Symposium of the AIME; "Columbium Metallurgy," Interscience Publishers, 1961.

13. R. T. Begley, "Development of Niobium-Base Alloys," WADC Technical Report 57-344, December 1958.

14. E. S. Tankins and R. Madden, "Effect of Grain Size, Strain Rate and Temperature on the Yield Strength of Columbium," 1960 Columbium Metallurgy Symposium of the AIME; "Columbium Metallurgy," Interscience Publishers, 1961.

15. E. T. Wessel, "Abrupt Yielding and the Ductile to Brittle Transition in Body-Centered-Cubic Metals," Journal of Metals 9, (930-8), 1957.

16. W. K. Klopp, "Oxidation Behavior and Protective Coatings for Columbium and Columbium-Base Alloys," Defense Metals Information Center Report #123, 15 Jan 1960.

17. A. G. Ingram, "Strain Aging of Refractory Metals," Defense Metals Information Center Report #134, 12 August 1960.

18. V. Cost and C. A. Wert, "Metal-Gas Equilibrium and the Niobium-Nitrogen Solid Solution," University of Illinois T. and A. M. Report No. 205, December 1961.

19. T. Hurlen, H. Kjllesdal, J. Markali, N. Norman, "Oxidation of Niobium," Technical (Scientific) Note #1, Contract #AF61-(052)-90, April 1959.

20. J. G. Morlet, H. H. Johnson and A. R. Troiano, "A New Concept of Hydrogen Embrittlement in Steel," Journal of the Iron and Steel Institute 189, (37-58), 1958.

21. A. L. Eustice and O. N. Carlson, "Hydrogen Embrittlement in Vanadium-Columbium Alloys" ASM Transactions 53, (501-510), 1961.

22. D. Weinstein, G. M. Sinclair and C. A. Wert, "The Strain Rate and Temperature Dependence of the Ductile to Brittle Transition in Molybdenum Subjected to Torsional Loading," Univ. of Ill. T. & A. M. Report No. 156, Dec. 1959, Contract AF 33 (616) - 5153.

23. P. E. Bennett and G. M. Sinclair, "An Analysis of the Time and Temperature Dependence of the Upper Yield Point in Iron," Univ. of Ill. T. & A. M. Report No. 157, Dec. 1959, Contract AF 33 (616) - 5153.

24. A. L. Eustice and O. N. Carlson, "The Effect of Hydrogen on the Properties of Iodide Vanadium," Trans. Met Soc AIME 221, (238-41), 1961.

25. B. F. Dyson, R. B. Jones and W. J. Mc. G. Tegart, "The Tensile Properties of High Purity Niobium at Low Temperatures," Journal of the Institute of Metals 87, (340), 1958-9.

26. Pages 165-181, "Methods of Testing Materials," Part 3, 1961 Book of AST Standards, American Society for Testing and Materials, Philadelphia, 1961.

27. Footnote, Page 166, Reference 26.

28. Metals Handbook, American Society for Metals, Cleveland, 1948.

29. J. R. Stephens, "Effect of Surface Condition on the Ductile-to-Brittle Transition Temperature of Tungsten," Technical Note D-676, National Aeronautics and Space Administration, Feb 1961.

30. Progress Report, Feb. 1961, Oklahoma University Research Institute, Project 1220; U. S. A. E. C. Contract AT-(40-1) -2570; and subsequent material. (Note: Also see Appendix to present report.)

31. H. C. Rogers, "The Tensile Fracture of Ductile Metals," Trans. Met Soc. AIME 218, (498-506), 1960.

32. S. Komjathy, "The Columbium-Hydrogen System," Armour Research Foundation Report 2120-5, May 1960.

33. J. Crank, "Mathematics of Diffusion," Oxford, Clarendon Press, 1956.

34. ENCYCLOPEDIA BRITANNICA, Encyclopaedia Brittanica Inc., 1958, p. 446.

35. HANDBOOK OF CHEMISTRY AND PHYSICS, 36th Edition, Chemical Rubber Publishing Company, Cleveland, 1954.

36. S. Dushman, "Scientific Foundations of Vacuum Technique," Wiley & Sons, New York, 1949.

37. D. Alpert, "New Developments in the Production and Measurement of Ultra High Vacuum," Journal of Applied Physics 24, (860-876), 1953.

38. E. S. Bartlett and J. A. Houck, "Physical and Mechanical Properties of Columbium and Columbium-Base Alloys," DMIC Report No. 125, February 1960.

39. H. C. Rogers, "The Mechanism of Crack Propagation in Ductile Metals," ACTA MET 7, (750-2), 1959.

40. A. L. Mincher & W. F. Sheely, "Effect of Structure and Purity on the Mechanical Properties of Columbium," Trans Met Soc AIME 221, (19-25), 1961.

41. H. Conrad, "On the Mechanism of Yielding and Flow in Iron," Journal of the Iron and Steel Institute 198, (364-75), 1961.

42. J. R. Low and R. W. Guard, "The Dislocation Structure of Slip Bands in Iron," Acta Met 7, (171-9), 1959.

43. private communication, F. J. Anders, du Pont de Nemours & Co, 1960.

44. H. W. Paxton, J. M. Sheehan & W. J. Babyak, "Observations on the Niobium-Hydrogen System," Trans Met Soc AIME 215, (725-7), 1959.

APPENDIX

APPENDIX

DATA SUMMARY

This appendix presents the analysis, history, annealing and hydrogenation treatments, and resultant tensile properties of the columbium used in this investigation. Tables 1 through 9 present this data for the first heat used, tables 10 through 19 present this data for the second heat used, and tables 20 through 41 present this data for the third heat used. Of tables 20 through 41, tables 20 through 30 pertain to standard tensile tests on third heat columbium stress relieved by an hour at 825°C, and tables 31 through 37 pertain to standard tensile tests on third heat columbium recrystallized by ½ hour, at 1200°C; tables 38 on pertain to prestrain and other types of test on third heat columbium.

The specimens are numbered within the heat consecutively according to position along the rods supplied by the DuPont Company. The treatments for the first heat were carried out on finished specimens, and for the second and third heats, on rods.

TABLE 1

CHEMICAL ANALYSIS, COLUMBIUM, HEAT NO. 1*
(DuPont Heat No. 129-005)

Analysis--PPM by Weight		
O 296	Fe < 50	Si < 50
H < 1	Cr < 30	B < .6
N 72	Ni < 30	Zr < 15
C 36	Ti < 30	Cr <130
	Ta 300	

*The material was received in the form of 0.4 inch diameter rod which had been extruded and swaged from a four inch diameter electron-beam-melted ingot. The ingot hardness was 61 BHN. The rod was in a 99 per cent cold worked condition. The chemical analysis was provided by DuPont.

TABLE 2

AMBIENT TEMPERATURE AS-RECEIVED TENSILE PROPERTIES*

Quantity	Specimen Number			
	1-7	1-2	1-3	1-4
Strain Rate, ipm/.75"	2.0	0.2	0.02	0.002
Proportional Limit, psi	--	64,900	62,600	55,200
.2% Yield Strength, psi	71,300	68,300	67,100	62,500
Tensile Strength, psi	71,300	69,000	67,100	65,500
Per Cent Elongation	23.1	24.2	22.4	21.8
Per Cent Reduction in Area	92.5	95.5	86	92.5
Fracture Strength, psi	282,000	420,000	158,000	284,000

*Four specimens of the first heat were tested at room temperature (approximately 27°C) at four different strain rates. The strain rate is indicated by the crosshead speed in the above table. The gage length of the tensile specimens was .75 in. The specimens were numbered according to position along the rods received from the supplier.

TABLE 3

LIQUID AIR AS-RECEIVED TENSILE PROPERTIES*

Quantity	Specimen Number				
	1-11	1-13	2-21	1-16	1-1
Strain Rate ipm/.75"	2.0	0.2	0.2	0.02	0.002
Proportional Limit, psi	--	122,000	126,000	118,700	108,000
0.2% Yield Strength, psi	142,000	138,700	133,500	136,500	125,000
Tensile Strength, psi	142,000	139,600	133,500	137,600	127,000
Per Cent Elongation	18.7	20.3	19.3	25.9	25.7
Per Cent Reducation in Area	76.5	75	71	71.5	76.5
Fracture Strength, psi	320,000	292,000	343,000	279,000	278,000

*Five specimens of the first heat were tested in liquid air at four strain rates. The testing temperature was approximately -190°C as measured by a thermocouple suitably placed. The specimens had undergone no treatment other than that performed by the supplier. The strain rate is indicated by the crosshead speed in inches per minute. The gage length of the tensile specimens was .75".

TABLE 4

TESTS OF AS-RECEIVED COLUMBIUM AT ELEVATED TEMPERATURES*

Quantity	Specimen Number				
	1-15	1-8	1-12	1-14	1-10
Testing Temperature, °C	166	254	254	254	393
Strain Rate, ipm/.75"	0.02	0.2	0.02	0.002	0.02
Proportional Limit, psi	59,600	57,800	59,100	55,100	53,000
0.2% Yield Strength, psi	65,300	61,500	64,100	63,700	58,900
Tensile Strength, psi	65,400	63,000	66,400	66,600	59,200
Per Cent Elongation	18.5	19.7	17.5	29.4	21.4
Per Cent Reduction in Area	91	92	87	90	93
Fracture Strength, psi	229,000	220,000	248,000	254,000	178,000

*Five specimens of columbium from the first heat were tested in the as-received condition at elevated temperatures. The strain rate is given as crosshead speed in inches per minute; the gage length of the specimens was .75".

TABLE 5

TENSILE PROPERTIES RESULTANT FROM 510°C, 1 HR AIR ANNEAL*

Quantity	Value
Strain Rate	0.02 ipm/.75"
Test Temperature	27°C
Proportional Limit, psi	52,800
0.2% Yield Strength, psi	58,300
Tensile Strength, psi	61,600
Per Cent Elongation	22.8
Per Cent Reduction in Area	94
Fracture Strength	324,000

* Specimen No. 2-18 was annealed an hour at 510°C in air. The resultant tensile properties are summarized.

TABLE 6

TENSILE PROPERTIES RESULTANT FROM "BAD VACUUM" CONTROL ANNEAL

Quantity	Specimen Number		
	2-16	2-17	2-19
Strain Rate, ipm/.75"	0.2	0.02	0.002
Proportional Limit, psi	51,100	53,800	54,100
0.2% Yield Strength, psi	56,400	57,500	57,100
Tensile Strength, psi	60,100	61,500	59,800
Per Cent Elongation	24.0	23.5	20.8
Per Cent Reduction in Area	92	93	88.5
Fracture Strength, psi	259,000	274,000	174,000

*Three specimens were annealed in a poor vacuum averaging 20 microns (for control purposes) at 510°C for 12 hours. The tensile properties resultant from this treatment are summarized in the above table. The test temperature was 27°C.

TABLE 7

TENSILE PROPERTIES RESULTANT FROM 2½ HR., 700°C VACUUM ANNEAL*

Quantity	Value
Proportional Limit, psi	43,700
0.2% Yield Strength, psi	47,700
Tensile Strength, psi	53,600
Per Cent Elongation	29.5
Per Cent Reduction in Area	91
Fracture Strength	208,000

*Specimen No. 2-20 was annealed for 2½ hours in high vacuum at 700°C. The tensile properties resultant from this treatment are summarized in this table. The strain rate employed was 0.02 ipm/.75". The test temperature was 27°C.

TABLE 8

TENSILE PROPERTIES RESULTING FROM ONE HR., 825°C VACUUM ANNEAL

Quantity	Specimen Number						
	2-1	2-3	2-5	2-6	2-7	2-2	2-4
Test Temperature, °C	28	28	28	28	-185	-187	-187
Strain Rate, ipm/.75"	0.2	0.2	0.02	0.002	0.2	0.02	0.002
Upper Yield Strength, psi	43,300	44,300	42,900	41,400	116,400	105,000	105,000
Lower Yield Strength, psi	40,500	40,500	40,100	39,200	108,000	98,300	99,000
Tensile Strength, psi	49,500	48,800	48,100	47,100	116,400	105,000	105,000
Per Cent Elongation	39.2	34.1	32.0	33.1	21.9	21.5	25.5
Per Cent Reduction in Area	96	91	92	92	84.5	84	85.5
Fracture Strength, psi	250,000	160,000	135,000	143,000	306,000	291,000	275,000

*Seven specimens were annealed for 1 hr. at 825°C in high vacuum. The tensile properties resultant from this treatment are summarized in this table.

TABLE 9

TENSILE PROPERTIES RESULTANT FROM THE PRELIMINARY HYDROGENATION TREATMENT

Quantity	Specimen Number							
	2-15	2-12	2-11	2-9	2-8	2-13	2-10	2-14
Test Temperature, °C	29	29	29	-185	-185	-185	28	28
Strain Rate, ipm/.75"	0.2	0.02	0.002	0.2	0.02	0.002	0.02	0.02
Proportional Limit, psi	55,000	55,000	52,000	fractured	108,000	98,600	53,600	54,900
0.2% Yield Strength, psi	fractured	57,000	fractured	fractured	fractured	120,000	58,200	57,600
Tensile Strength, psi	57,000	57,500	55,500	118,000	122,000	122,500	62,000	61,000
Per Cent Elongation	0	0	0	0	0	0	5.1	4.1
Per Cent Reduction in Area	0	0	0	0	0	0	4.6	9.0
Fracture Strength, psi	57,000	57,500	55,500	118,000	122,000	122,500	65,000	66,500

*Eight specimens from the first heat were subjected to a hydrogen atmosphere for six hours at 510°C. The resultant average hydrogen concentration was 640 ppm. The hydrogen contents and distributions for the individual specimens varied as the specimens were strung out to obtain a nonuniform temperature. In addition, two of the specimens hydrogenated were turned down on a lathe. Specimen No. 2-10 was turned down 11% by diameter and Specimen No. 2-14 was turned down 43%. This machining treatment increased the very low ductility otherwise observed for these hydrogenated specimens.

TABLE 10

ANALYSIS OF SECOND HEAT OF COLUMBIUM*
(DuPont Heat No. T-35-S)

Analysis--PPM by Weight					
O	180	Fe	< 50	Ta	490
H	2	Cr	< 30	Si	≤ 50
N	32	Ni	< 30	B	< 0.7
C	9	Ti	60	Cu	< 130
				Zr	< 100

*The processing of the columbium was as follows. The columbium, originally in a 3" diameter electron beam melted ingot, was swaged at 1100°C down to a diameter of 1". The 1" rod was then machined to remove oxide, and swaged at room temperature down to a diameter of 3/8". The ingot hardness was 69 BHN.

TABLE 11

AS-RECEIVED TENSILE PROPERTIES OF THE SECOND HEAT*

Quantity	Specimen Number		
	28	29	30
Test Temperature Degrees Centigrade	-75	27	202
Proportional Limit, psi	45,300	38,750	36,600
0.2% Yield Strength, psi	55,200	45,700	43,600
Tensile Strength, psi	61,800	48,700	44,700
Per Cent Reduction in Area	91	97	97
Per Cent Elongation	23	20	17
Fracture Strength, psi	269,000	405,000	--

*Three specimens of the second heat were tested in the as-received condition. The tensile properties of this material are summarized in this table. Specimen numbers apply to second heat. The strain rate employed for the whole second heat was 0.02 ipm/.815".

TABLE 12

TENSILE PROPERTIES, SECOND HEAT, 126 PPM HYDROGEN*

Quantity	Specimen Number			
	15	13	16	14
Test Temperature, Degrees Cent.	-191	27	64	123
Proportional Limit, psi	106,500	37,100	33,600	34,500
0.2% Yield Strength, psi	119,000	41,600	37,700	38,600
Tensile Strength, psi	123,000	48,400	42,800	41,800
Per Cent Reduction in Area	3	87	94	98
Per Cent Elongation	3	25	25	22
Fracture Strength, psi	127,000	203,000	231,000	437,000

*The tensile properties of columbium of the second heat that was hydrogenated to a uniform hydrogen content of 126 ppm are summarized. The additional history is 2.3 hrs. at 536°C concurrent to hydrogenation. The strain rate employed was 0.02 ipm/.815".

TABLE 13

TENSILE PROPERTIES, SECOND HEAT, 147 PPM HYDROGEN*

Quantity	Specimen Number			
	18	19	20	17
Test Temperature, Degrees Cent.	-185	-75	27	121
Proportional Limit, psi	102,000	40,800	37,000	32,400
0.2% Yield Strength, psi	116,500	49,200	41,800	37,400
Tensile Strength, psi	121,000	57,100	48,600	40,100
Per Cent Reduction of Area	4	5	42	95
Per Cent Elongation	1	2	14	20
Fracture Strength, psi	121,000	61,000	77,000	167,000

*The tensile properties of columbium of the second heat that was hydrogenated to a uniform hydrogen content of 147 ppm are summarized. The additional history is 1.7 hrs. at 536°C concurrent to hydrogenation. The strain rate employed was 0.02 ipm/.815".

TABLE 14

TENSILE PROPERTIES, SECOND HEAT, 220 PPM HYDROGEN

Quantity	Specimen Number			
	11	12	9	10
Test Temperature, Degrees Cent.	-190	-79	27	204
Proportional Limit, psi	--	38,300	35,100	33,200
0.2% Yield Strength, psi	--	50,100	40,000	38,200
Tensile Strength, psi	--	58,900	48,500	40,300
Per Cent Reduction in Area	3	1	23	99
Per Cent Elongation	3	2	16	19.5
Fracture Strength, psi	--	59,000	63,000	--

*The tensile properties of columbium of the second heat that was hydrogenated to a uniform hydrogen content of 220 ppm are summarized. The additional history is 2.9 hrs. at 533°C concurrent to hydrogenation. The strain rate employed was 0.02 ipm/.815".

TABLE 15

TENSILE PROPERTIES, STRESS RELIEVED, SECOND HEAT, 399 PPM HYDROGEN*

Quantity	Specimen Number			
	8	5	6	7
Test Temperature, Degrees Cent.	-189	-79	27	127
Proportional Limit, psi	92,100	31,400	20,100	16,600
0.2% Yield Strength, psi	--	39,000	25,400	19,300
Tensile Strength, psi	96,100	44,800	38,600	28,500
Per Cent Reduction in Area	0	5	23	92
Per Cent Elongation	1	1.5	23.5	37
Fracture Strength, psi	96,000	47,000	50,000	144,000

*The tensile properties of stress relieved columbium of the second heat that was hydrogenated to a hydrogen content of 399 ppm are summarized. The additional history is 2.7 hrs. at 795°C (stress relief anneal) followed by 4¼ hrs. at 536°C, concurrent to hydrogenation. The strain rate employed was 0.02 ipm/.815".

TABLE 16

TENSILE PROPERTIES, STRESS RELIEVED, SECOND HEAT, 655 PPM HYDROGEN*

Quantity	Specimen Number		
	4	3	2
Test Temperature, Degrees Centigrade	-77	27	130
Proportional Limit, psi	32,600	19,100	14,350
0.2% Yield Strength, psi	38,900	22,200	17,300
Tensile Strength, psi	40,400	36,250	27,400
Per Cent Reduction in Area	0	16	84
Per Cent Elongation	1	17	30
Fracture Strength, psi	41,000	44,000	97,000

*The tensile properties of stress relieved columbium of the second heat that was hydrogenated to a uniform hydrogen content of 655 ppm are summarized in this table. The additional history is 3.0 hrs. at 800°C (stress relief anneal) followed by 3.0 hrs. at 498°C, concurrent to hydrogenation. The strain rate employed was 0.02 ipm/.815".

TABLE 17

TENSILE PROPERTIES, SECOND HEAT, 669 PPM HYDROGEN*

Quantity	Specimen Number			
	24	26	27	25
Test Temperature, Degrees Cent.	-76	27	65	120
Proportional Limit, psi	41,500	36,300	33,800	33,600
0.2% Yield Strength, psi	52,500	42,500	40,600	39,000
Tensile Strength, psi	60,800	52,200	47,200	42,900
Per Cent Reduction in Area	0	21	33	75
Per Cent Elongation	1	14	19	18
Fracture Strength, psi	61,000	65,000	57,000	73,000

*The tensile properties of columbium of the second heat that was hydrogenated to a uniform hydrogen content of 669 ppm are summarized. The additional history is 2¼ hrs. at 522°C, concurrent to hydrogenation. The strain rate employed was 0.02 ipm/.815".

TABLE 18

TENSILE PROPERTIES, SECOND HEAT, HYDROGENATED AND DEHYDROGENATED*

Quantity	Specimen Number		
	21	22	23
Test Temperature, Degrees Centigrade	-191	27	121
Proportional Limit, psi	108,000	33,500	32,100
0.2% Yield Strength, psi	118,000	38,200	36,700
Tensile Strength, psi	118,000	45,200	40,500
Per Cent Reduction of Area	78	96	100
Per Cent Elongation	19	23	20
Fracture Strength, psi	230,000	345,000	--

*Specimens Nos. 21, 22 and 23 of the second heat were hydrogenated to 930 ppm, in which condition they were too brittle to take a thread. They were subsequently dehydrogenated by high vacuum anneal to under 2 ppm and tested in the dehydrogenated condition. The tensile properties resultant from this treatment are summarized in this table. The additional history is 3.7 hrs. at 594°C, concurrent to hydrogenation and 12 hrs. at 603°C concurrent to dehydrogenation. The strain rate employed was 0.02 ipm/.815".

TABLE 19

TENSILE PROPERTIES, SECOND HEAT, ANNEALED AT 700°C FOR 2¼ HOURS*

Quantity	Value
Proportional Limit, psi	27,600
0.2% Yield Strength, psi	31,000
Tensile Strength, psi	38,500
Per Cent Elongation	28

*Specimen No. 1 of heat two was annealed 2¼ hrs. at 697°C. The hydrogen content was well under 2 ppm. The test temperature was 27°C and the strain rate 0.02 ipm/.815". The tensile properties are summarized.

TABLE 20

ANALYSIS OF DUPONT HEAT D-1190*

Element	Content in ppm by weight
Oxygen	206
Nitrogen	50 or less
Carbon	50
Iron	122
Nickel	75
Chromium	10 or less
Copper	10 or less

Approximate history of DuPont heat D-1190
1) Extruded warm from 3" round to 3/4" round.
2) Swaged from 3/4" round to 3/8" round at room temperature.

*The hydrogen content of heat D-1190 was not given, but from the other analyses is 1-2 ppm. This hydrogen content applies to the three as-received specimens tested; the stress-relieved and recrystallized material was dehydrogenated by these treatments to hydrogen contents below ½ ppm.

TABLE 21

TENSILE PROPERTIES OF AS-RECEIVED THIRD HEAT COLUMBIUM*

Quantity	Specimen Number		
	104	103	105
Test Temperature Degrees Centigrade	-192	24	126
Proportional Limit, psi	119,300	59,200	54,300
0.2% Yield Strength, psi	129,500	67,500	61,400
Tensile Strength, psi	137,000	75,700	66,000
Per Cent Reduction in Area	71.5	92	93
Per Cent Elongation	21.5	19	15
Fracture Strength, psi	273,000	302,000	246,000

*Three as-received specimens of the third heat were tested. The hydrogen content was 1-2 ppm. The tensile properties resultant are summarized in this table. The strain rate employed was 0.02 ipm/.815".

TABLE 22

TENSILE PROPERTIES, THIRD HEAT STRESS RELIEVED PURE COLUMBIUM*

Specimen No.	Strain Rate, ipm/.815"	Test Temperature, °C	Proportional Limit, psi	0.2% Yield Strength, psi	Tensile Strength, psi	Per Cent Reduction in Area	Per Cent Elongation	Fracture Strength, psi
51	0.002	-193	102,800	112,000	115,000	76	23	247,000
81	0.002	-77	48,500	52,400	64,000	90	27	240,000
49	0.002	21	43,100	47,000	62,100	92	24	243,000
82	0.002	129	38,800	44,100	55,200	92	20	252,000
84	0.2	-193	112,700	121,500	123,600	75.5	20	266,000
83	0.2	-76	60,300	63,300	73,500	77	32	111,000
50	0.2	28	44,900	48,300	62,000	93	27	274,000
79	0.2	116	42,500	46,600	57,900	92	23	236,000
97	2.0	27	--	49,100	61,700	94	28	--
54	0.02	-193	108,000	117,000	122,000	71.5	21	243,000
100	0.02	29	43,100	45,700	57,700	93	29	236,000

TABLE 22--Continued

Specimen No.	Strain Rate, ipm/.815"	Test Temperature, °C	Proportional Limit, psi	0.2% Yield Strength, psi	Tensile Strength, psi	Per Cent Reduction in Area	Per Cent Elongation	Fracture Strength, psi
80	0.02	27	41,800	46,000	57,700	92.5	23.5	243,000
53	0.02	116	40,000	43,900	55,200	90	20.5	200,000

*Thirteen specimens of the third heat were stress relieved an hour at 825°C in high vacuum. The hydrogen content was under ½ ppm. The tensile properties resultant from this treatment are summarized in this table.

TABLE 23

STRESS RELIEVED COLUMBIUM TENSILE PROPERTIES, THIRD HEAT, HYDROGENATED TO 19 ± ½ PPM

Quantity	Specimen Number					
	73	76	75	78	74	77
Strain Rate, ipm/.815"	0.02	0.20	0.02	0.02	0.02	0.02
Test Temperature, °C	-193	-76	0	27	79	132
Proportional Limit, psi	123,000	59,500	44,400	42,000	42,300	42,100
0.2% Yield Strength, psi	129,300	62,600	47,800	46,700	46,100	44,800
Tensile Strength, psi	130,500	66,800	63,600	60,600	57,300	55,400
Per Cent Reduction in Area	56.5	18.5	89	91.5	92	92
Per Cent Elongation	22.5	17.5	28	26	20.5	20.5
Fracture Strength, psi	232,000	46,000	233,000	240,000	230,000	230,000

*Six specimens of the third heat stress relieved materials were hydrogenated to a uniform hydrogen content of 19 ± ½ ppm by weight. The additional history is 1 hr. at 825°C (stress relief) followed by 8 hours at 445°C (hydrogenation). The tensile properties resultant from this treatment are summarized in this table.

TABLE 24

TENSILE PROPERTIES, STRESS RELIEVED THIRD HEAT COLUMBIUM, HYDROGENATED TO 43 PPM*

Quantity	Specimen Number					
	72	70	67	71	68	69
Strain Rate, ipm/.815"	0.02	0.02	0.02	0.02	0.02	0.02
Test Temperature, Degrees Centigrade	-193	-74	0	25	79	131
Proportional Limit, psi	124,500	59,500	43,600	46,900	39,300	41,100
0.2% Yield Strength, psi	133,000	62,300	47,500	49,500	43,500	45,100
Tensile Strength, psi	135,000	66,300	63,400	64,000	57,000	56,800
Per Cent Reduction in Area	52	7.5	80	91.5	90	91
Per Cent Elongation	16	1.5	26	31.5	20.5	21.5
Fracture Strength, psi	222,000	71,000	169,000	255,000	213,000	236,000

*Six specimens of the third heat stress relieved material were hydrogenated to a uniform hydrogen content of 43 ppm by weight. The additional history is 1 hr. at 825°C (stress relief) followed by 16 hours at 450°C (hydrogenation). The tensile properties resultant from this treatment are summarized in this table.

TABLE 25

TENSILE PROPERTIES, STRESS RELIEVED THIRD HEAT COLUMBIUM, HYDROGENATED TO 70 PPM*

Quantity	Specimen Number				
	42	44	45	41	43
Strain Rate, ipm/.815"	0.002	0.002	0.002	0.2	0.2
Test Temperature, °C	-193	-77	27	-72	27
Proportional Limit, psi	106,400	53,600	42,000	60,500	42,100
0.2% Yield Strength, psi	117,300	56,600	44,700	65,500	47,300
Tensile Strength, psi	124,000	61,200	59,200	66,600	63,800
Per Cent Reduction in Area	9	9.5	88.5	11	82.5
Per Cent Elongation	5	1.5	25.5	2	30.5
Fracture Strength, psi	136,000	68,000	210,000	75,000	180,000

*Five specimens of the third heat stress relieved material were hydrogenated to a uniform hydrogen content of 70 ppm by weight. The additional history is 1 hr. at 825°C (stress relief) followed by 7 hrs. at 540°C (hydrogenation). The tensile properties resultant from this treatment are summarized in this table.

TABLE 26

TENSILE PROPERTIES, STRESS RELIEVED THIRD HEAT COLUMBIUM, HYDROGENATED TO 98½ PPM*

Quantity	Specimen Number		
	62	63	65
Strain Rate, ipm/.815"	0.02	0.02	0.02
Test Temperature, Degrees Centigrade	-193	-77	29
Proportional Limit, psi	115,000	58,500	42,100
0.2% Yield Strength, psi	133,000	62,100	46,500
Tensile Strength, psi	140,000	63,600	61,900
Per Cent Reduction in Area	2	11	77
Per Cent Elongation	1	1.5	25.5
Fracture Strength, psi	143,000	71,500	143,000

*Three specimens of the third heat stress relieved material were hydrogenated to a uniform hydrogen content of 98½ ppm by weight. The additional history is 1 hr. at 825°C (stress relief) followed by 37½ hrs. at 480°C (hydrogenation). The tensile properties resultant from this treatment are summarized in this table.

TABLE 27

TENSILE PROPERTIES, STRESS RELIEVED THIRD HEAT COLUMBIUM, HYDROGENATED TO 151½ PPM*

Quantity	Specimen Number		
	57	59	56
Strain Rate, ipm/.815"	0.02	0.02	0.20
Test Temperature, Degrees Centigrade	-194	-76	29
Proportional Limit, psi	105,600	51,900	--
0.2% Yield Strength, psi	124,900	58,900	47,800
Tensile Strength, psi	134,000	65,100	66,100
Per Cent Reduction in Area	3	9	53
Per Cent Elongation	1.5	1.5	24.5
Fracture Strength, psi	138,000	71,000	--

*Three specimens of the third heat stress relieved material were hydrogenated to a uniform hydrogen content of 151½ ppm by weight. The additional history is 1 hr. at 825°C (stress relief) followed by 17 hrs. at 510°C (hydrogenation). The tensile properties resultant from this treatment are summarized in this table.

TABLE 28

TENSILE PROPERTIES, STRESS RELIEVED THIRD HEAT COLUMBIUM, HYDROGENATED TO 252 PPM HYDROGEN*

Quantity	Specimen Number				
	66	47	48	46	60
Strain Rate, ipm/.815"	0.002	0.002	0.002	0.20	0.20
Test Temperature, °C	-193	-76	27	-75	29
Proportional Limit, psi	94,900	45,300	42,100	50,000	45,600
0.2% Yield Strength, psi	115,400	53,800	44,000	61,500	48,800
Tensile Strength, psi	128,000	58,600	58,200	68,700	55,000
Per Cent Reduction in Area	2	4.5	16	6.5	8.5
Per Cent Elongation	2	0.5	9	1.5	2.5
Fracture Strength, psi	131,000	61,300	69,000	73,500	60,500

*Five specimens of the third heat stress relieved material were hydrogenated to a uniform hydrogen content of 252 ppm by weight. The additional history is 1 hr. at 825°C (stress relief) followed by 6 hrs. at 540°C (hydrogenation). The tensile properties resultant from this treatment are summarized in this table.

TABLE 29

TENSILE PROPERTIES, STRESS RELIEVED THIRD HEAT COLUMBIUM, HYDROGENATED TO 455 PPM HYDROGEN*

Quantity	Specimen Number					
	87	85	89	86	88	90
Strain Rate, ipm/.815"	0.02	0.02	0.02	0.020	0.002	2.0
Test Temperature, °C	-75	22	30	114	22	27
Proportional Limit, psi	46,800	42,100	37,200	39,300	42,600	--
0.2% Yield Strength, psi	56,500	45,500	40,000	43,000	47,800	--
Tensile Strength, psi	57,500	51,500	53,500	54,500	54,600	--
Per Cent Reduction in Area	4	9	6	77	9	8
Percent Elongation	0.5	2	5.5	19.5	2	0.5
Fracture Strength, psi	60,100	56,800	57,100	130,000	60,300	--

*Six specimens of the third heat stress relieved material were hydrogenated to a uniform hydrogen content of 455 ppm by weight. The additional history is 1 hr. at 825°C (stress relief) followed by two days at 450°C (hydrogenation, four increments).

TABLE 30

HIGH STRAIN RATE TENSILE PROPERTIES, VARIOUS HYDROGEN CONTENTS, THIRD HEAT STRESS RELIEVED COLUMBIUM[a]

Quantity	Specimen Number		
	94	101	38
Time-Temperature of Hydrogenation	b	b	c
Hydrogen Content, ppm by Weight	41½	41½	72
Test Temperature, Degrees Centigrade	-191	-74	-191
0.2% Yield Strength, psi	137,800	71,900	132,400
Tensile Strength, psi	141,800	71,900	137,800
Per Cent Reduction in Area	54	6.5	3
Per Cent Elongation	14	5.5	1.5
Fracture Strength, psi	--	69,000	142,000

[a]Additional hydrogenated specimens of third heat stress relieved columbium were tested at a strain rate of 2.0 ipm/ .815". All three were stress relieved 1 hr. at 825°C. The tensile properties are summarized in this table.

[b]8 hrs. at 460°C.

[c]3½ hrs. at 520°C.

TABLE 31

TENSILE PROPERTIES, RECRYSTALLIZED THIRD HEAT COLUMBIUM, LESS THAN ONE HALF PPM HYDROGEN*

Specimen No.	Strain Rate, ipm/.815"	Test Temperature, °C	Proportional Limit, psi	0.2% Yield Strength, psi	Upper Yield Strength, psi	Lower Yield Strength, psi	Tensile Strength, psi	Per Cent Reduction in Area	Per Cent Elongation	Fracture Strength, psi
1	0.002	-194	92,600	101,000	--	--	104,000	67	21	178,000
33	0.002	-76	--	--	42,700	39,800	52,700	93	44.5	263,000
31	0.002	28	--	--	28,500	25,700	38,300	95.5	44	216,000
32	0.02	-193	100,300	107,000	--	--	109,300	72	23	206,000
4	0.02	-76	--	--	44,600	44,100	54,100	88	35.5	180,000
7	0.02	27	--	--	26,800	25,300	37,000	91.5	45	119,000
5	0.2	-193	94,300	107,200	--	--	112,400	52.5	18.5	174,000
34	0.2	-75	--	--	52,000	49,100	57,100	91	43.5	195,000
35	0.2	28	--	--	31,000	26,100	37,900	93.5	46	147,000

*Ten specimens of the third heat recrystallized columbium with a hydrogen content of less than ½ ppm were tested at various strain rates. The additional history is ½ hr. at 1200°C (recrystallization). The tensile properties resultant from this treatment are summarized in this table.

TABLE 32

NOTCH TENSILE PROPERTIES, RECRYSTALLIZED PURE THIRD HEAT COLUMBIUM*

Quantity	Value
Specimen Number	3
Crosshead Speed	0.20 ipm
Test Temperature, °C	28
Stress of First Measurable Strain	41,700 psi
Tensile Strength	63,000 psi
Percent Reduction of Area, Based on 0.162" Diameter	87
Percent Elongation, Based on 1.12" Smooth Section	12
Fracture Strength	73,000 psi

*Specimen No. 3 of the third heat columbium recrystallized by ½ hr. at 1200°C, with hydrogen content below ½ ppm, was used to obtain the notch-tensile properties of this material. The notch diameter was .162", the notch radius 0.008" and the angle 60°. The smooth section diameter was .225". The tensile strength ratio (to the unnotched average) was 1.68, characteristic of great ductility, which was also indicated by the extensive deformation of the straight section. The notch-tensile properties derived from this specimen are summarized in this table.

TABLE 33

TENSILE PROPERTIES, RECRYSTALLIZED THIRD HEAT COLUMBIUM, FOUR AND ONE HALF PPM HYDROGEN

Quantity	Specimen Number		
	12	28	25
Strain Rate, ipm/.815"	0.2	0.2	0.02
Test Temperature, Degrees Centigrade	-193	-78	28
Proportional Limit, psi	103,000	--	--
Upper Yield Strength, psi	--	54,700	26,500
0.2% Yield Strength, psi	110,700	--	--
Lower Yield Strength, psi	--	51,400	25,800
Tensile Strength, psi	116,000	63,500	--
Per Cent Reduction in Area	4	72.5	--
Per Cent Elongation	2.5	40	--
Fracture Strength, psi	120,700	140,500	--

*Three specimens of the third heat recrystallized columbium with a hydrogen content of four and ½ ppm were tested at various strain rates. The additional history is ½ hr. at 1200°C (recrystallization) followed by 24 hrs. at 655°C (hydrogenation). The tensile properties resultant from this treatment are summarized in this table.

TABLE 34

TENSILE PROPERTIES, RECRYSTALLIZED THIRD HEAT COLUMBIUM, EIGHT AND ONE HALF UNIFORM PPM HYDROGEN*

Quantity	Specimen Number				
	20	7	13	30	17
Strain Rate, ipm/.815"	0.002	0.002	0.020	0.2	0.2
Test Temperature, °C	-193	-77	28	-194	-77
Proportional Limit, psi	96,800	--	--	104,700	--
Upper Yield Strength, psi	--	40,400	27,000	--	53,800
0.2% Yield Strength, psi	106,200	--	--	115,500	--
Lower Yield Strength, psi	--	37,800	24,800	--	49,900
Tensile Strength, psi	109,900	50,600	--	120,700	62,100
Per Cent Reduction in Area	5	11.5	--	50	59
Fracture Strength, psi	114,100	57,300	--	193,000	108,500
Per Cent Elongation	4.5	10.5	--	19.5	37

*Five specimens of the third heat recrystallized columbium with a uniform hydrogen content of 8½ ppm were tested at various strain rates. The additional history is ½ hr. at 1200°C (recrystallization) followed by 48 hrs. at 600°C (hydrogenation). The tensile properties resultant from this treatment is summarized in this table.

TABLE 35

TENSILE PROPERTIES, RECRYSTALLIZED THIRD HEAT COLUMBIUM, FOURTEEN AND ONE THIRD PPM HYDROGEN*

Quantity	Specimen Number				
	24	27	6	8	23
Strain Rate, ipm/.815"	0.002	0.002	0.2	0.2	0.2
Test Temperature, °C	-185	-76	-188	-76	26
Proportional Limit, psi	102,000	--	104,000	--	--
Upper Yield Strength, psi	--	43,100	--	51,600	29,800
0.2% Yield Strength, psi	110,200	--	114,900	--	--
Lower Yield Strength, psi	--	39,800	--	49,200	28,400
Tensile Strength psi	113,500	45,400	120,300	51,600	43,000
Per Cent Reduction in Area	5	6	7.5	1.5	87
Per Cent Elongation	4	4.5	4	8	48
Fracture Strength psi	118,400	48,400	130,000	47,300	138,000

*Five specimens of the third heat recrystallized columbium with a uniform hydrogen content of 14 1/3 ppm were tested at various strain rates. The additional history is ½ hr. at 1200°C (recrystallization) followed by 10 hrs. at 570°C (hydrogenation). The results are summarized in this table.

TABLE 36

TENSILE PROPERTIES, RECRYSTALLIZED THIRD HEAT COLUMBIUM, THIRTY AND THREE FOURTHS PPM UNIFORM HYDROGEN*

Quantity	Specimen No.				
	19	11	9	29	18
Strain Rate, ipm/.815"	0.002	0.002	0.2	0.2	0.2
Test Temperature, °C	-76	26	-188	-76	26
Proportional Limit, psi	--	--	107,400	--	--
Upper Yield Strength, psi	39,400	24,600	--	56,300	30,400
0.2% Yield Strength, psi	--	--	118,900	--	--
Lower Yield Strength, psi	38,900	23,300	--	52,200	28,800
Tensile Strength psi	40,900	38,400	126,500	56,300	44,300
Per Cent Reduction in Area	7	89	4.5	4.5	84.5
Per Cent Elongation	2	51½	2.5	4	42
Fracture Strength, psi	44,500	133,000	132,000	59,000	136,000

*Five specimens of the third heat recrystallized columbium with a uniform hydrogen content of 30 3/4 ppm were tested at various strain rates. The additional history is ½ hr. at 1200°C (recrystallization) followed by 18 hrs. at 550°C (hydrogenation). The tensile properties resultant from this treatment are summarized in this table.

TABLE 37

TENSILE PROPERTIES, RECRYSTALLIZED THIRD HEAT COLUMBIUM, SIXTY-FOUR PPM UNIFORM HYDROGEN[a]

Quantity	Specimen Number				
	16[b]	15	10	22	14
Strain Rate, ipm/.815"	0.002	0.002	0.2	0.2	0.2
Test Temperature, °C	-193	-76	-193	-76	27
Proportional Limit, psi	--	--	105,000	--	--
Upper Yield Strength, psi	--	41,800	--	55,600	30,600
0.2% Yield Strength, psi	--	--	118,200	--	--
Lower Yield Strength, psi	--	41,100	--	54,400	29,600
Tensile Strength, psi	77,800	42,600	125,600	55,600	43,900
Per Cent Reduction in Area	0	8	2	8.5	79.5
Per Cent Elongation	0	2	1	2	44.5
Fracture Strength psi	77,800	46,400	128,500	59,200	114,000

[a]Five specimens of the third heat recrystallized columbium with a uniform hydrogen content of 64 ppm were tested at various strain rates. The additional history is ½ hr. at 1200°C (recrystallization) followed by 42 hrs. at 525°C (hydrogenation).

[b]Specimen No. 16 broke in the fillet--there were circumferential tool marks.

TABLE 38

TENSILE PROPERTIES, STEP COOLING TEST*

Quantity	Value
Strain Rate, ipm/.815"	0.02
Test Temperature, degrees Cent.	-192
Proportional Limit, psi	116,300
0.2% Yield Strength, psi	134,000
Tensile Strength, psi	135,900
Per Cent Reduction in Area	48
Per Cent Elongation	29
Fracture Strength, psi	238,000

*Specimen No. 93 of the stress relieved third heat material hydrogenated to 41½ ppm uniform hydrogen content was utilized in a step cooling test. Dry ice chunks were placed about the specimen and Solox poured in. Then, after several minutes, the dry ice and Solox was poured out and immediately replaced by liquid air. After cessation of bubbling the specimen was pulled. The tensile properties resultant from this treatment are summarized.

TABLE 39

TENSILE PROPERTIES DERIVED FROM PRESTRAIN TESTS[a]

Quantity	Specimen Number		
	102[b]	99	98
Strain Rate, ipm/.815"	0.02	0.02	0.20
Upper Test Temperature, °C	27	27	27
Proportional Limit, psi-27°C	--	44,400	42,500
0.2% Yield Strength, psi-27°C	--	--	46,000
Amount of Prestrain (Per Cent Elongation	0.0	0.075	1.07
Lower Test Temperature, °C	-191	-191	-191
Tensile Strength, Lower Test Temperature, psi	136,700	136,200	137,500
Fracture Strength, Lower Test Temperature, psi	229,000	139,600	139,400
Per Cent Reduction in Area	53	3	1
Per Cent Elongation	21	3	1

[a]Nine specimens of various conditions and hydrogen contents were strained various amounts at room temperature and subsequently pulled to failure in liquid air. The percent reduction in area and the percent elongation pertain to the lower temperature alone, the diameter of the gage section having been remeasured after prestrain. The material was stress relieved by annealing 1 hr. at 825°C in high vacuum. Afterward the material was annealed 8 hrs. at 460°C in the course of hydrogenation to a uniform hydrogen content of 41½ ppm.

[b]Specimen No. 102 was stressed to 40,000 psi, below or at the proportional limit; there was no plastic strain.

TABLE 40

TENSILE PROPERTIES DERIVED FROM PRESTRAIN TESTS[a]

Quantity	Specimen Number	
	91	96
Condition	b	b
Hydrogen Content (Uniform), ppm by Weight	41½	41½
Time-Temperature of Hydrogenation	8 hrs.-460°C	8 hrs.-460°C
Strain Rate, ipm/.815"	0.20	0.02
Upper Test Temperature, Degrees Centigrade	27	27
Proportional Limit, psi-27°Cent.	43,200	43,200
0.2% Yield Strength, psi-27°C	45,800	46,400
Amount of Prestrain (Per Cent Elongation)	3.15	9.5
Lower Test Temperature, Degrees Centigrade	-191	-193
Tensile Strength, psi, Lower Test Temperature	139,800	141,500
Fracture Strength, psi, Lower Test Temperature	145,200	148,000
Percent Reduction in Area	4	4.5
Percent Elongation	1.5	0.5

[a]The percent reduction in area and the percent elongation pertain to the lower temperature alone, the diameter of the gage section having been remeasured after prestrain.

[b]Stress relieved at 1 hr.-825°C.

TABLE 41

TENSILE PROPERTIES DERIVED FROM PRESTRAIN TESTS[a]

Quantity	Specimen Number			
	92	36	55	21
Condition	b	b	b	c
Hydrogen Content, Uniform, ppm by Weight	½ or less	72	151½	less than ½
Strain Rate, ipm/.815"	0.02	0.02	0.02	0.02
Upper Test Temperature, Degrees Centigrade	27	27	27	27
Proportional Limit, psi, 27°C	41,200	42,600	42,800	--
0.2% Yield Strength, psi 27°C	45,100	45,600	46,500	--
Amount of Prestrain, (Percent Elongation)	10.58	4.78	3.33	13
Lower Test temperature, Degrees Centigrade	-190	-189	-192	-190
Tensile Strength, Lower Temperature	123,300	137,000	137,000	115,000
Fracture Strength, Lower Temperature	249,000	139,500	138,400	192,000

TABLE 41--Continued

Quantity	Specimen Number			
	92	36	55	21
Percent Reduction in Area	75	2	1	66
Percent Elongation	19.5	1	1.5	17.5

[a]The percent reduction in area and the percent elongation pertain to the lower temperature alone, the diameter of the gage section having been measured after prestrain.

[b]Stress relieved by 1 hr. at 825°C.

[c]Recrystallized at ½ hr. at 1200°C.

Test for Delayed Failure

One pure and three hydrogenated (455 ppm) stress relieved specimens were tested for delayed failure at room temperature. The crosshead was stopped just before the specimen might be expected to break in the course of the conventional tensile test. In an hour near the maximum load of the conventional tensile test, failure did not occur. Instead an asymptotic decrease in load amounting to several percent occurred. Stopping the crosshead before yield resulted in relatively no load drop, demonstrating that the load drop resulted from plastic flow in the specimen. Delayed failure, however, may occur in hydrogenated high-strength columbium alloys, as an increase in yield strength and the structural changes which bring it about may introduce different fracture mechanisms.